# Evaluation and Improvement of Methods for the Sampling and Analysis of Selected Toxic Air Contaminants

to

California Air Resources Board

April 1989

Battelle

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Volume 2

Final Report

FINAL REPORT

(VOLUME 2)

on

EVALUATION AND IMPROVEMENT OF METHODS FOR THE
SAMPLING AND ANALYSIS OF SELECTED
TOXIC AIR CONTAMINANTS

to

CALIFORNIA AIR RESOURCES BOARD

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by

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PROJECT SUMMARY

Assembly Bill 1807 (Tanner) directs the California Air Resources Board (ARB) to identify and monitor the concentrations of selected toxic air contaminants (TACs) present in the ambient atmosphere. For most of these TACs, the ambient concentrations are generally less than one part-per-billion per compound (24-hour time integrated samples). The use and improvement of current sampling and analysis methods for determining these contaminants are being carried out by the ARB, the U.S. Environmental Protection Agency, local districts and independent contractors.

PROJECT OBJECTIVES

The objective of this project is to examine the materials and methods presently being used by the ARB to sample and analyze TACs. The advantages and disadvantages of the present methods are to be documented by field and laboratory analyses. Alternative materials and methods are to be recommended in those cases where serious disadvantages can be corrected. Experimental data must be obtained to demonstrate superiority of alternative approaches.

The specific TACs to be studied include the following:

chloroethene	1,2-dibromoethane
1,1-dichloroethene	tetrachloroethene
dichloromethane	benzene
trichloromethane	toluene
1,2-dichloroethane	m-xylene
1,1,1-trichloroethane	o-xylene
tetrachloromethane	p-xylene
trichloroethene	

Two additional halogenated organic compounds, dichlorodifluoromethane (freon-12) and trichlorotrifluoroethane (freon-113) are also to be included because they are good indicators of urban pollutant build-up.

BATTELLE'S APPROACH

Battelle's examination and evaluation of existing and alternative sampling and analysis methodologies involved laboratory studies conducted at Battelle, statistical analyses of ARB's field and laboratory data, and a field study in Bakersfield, California. Our project results are presented in two volumes. Volume 1 contains five chapters as follows:

Chapter I - Storage and Transportation Effects on TAC Concentrations in Tedlar Bags and Stainless Steel Canisters

Chapter II - Evaluation of Selected Whole Air Sampling Devices

Chapter III - Evaluation of ARB's Analytical Method-ADDL002

Chapter IV - Alternative Analytical Approaches

Chapter V - Evaluation of ARB Quality Control Procedures

Volume 2 contains Battelle's laboratory studies and statistical analyses of ARB data. The laboratory studies include the Tedlar bag permeation studies and bag/can storage studies at zero and 0.5 ppb TAC concentrations. Statistical analysis of ARB data includes the bag swap and bag/can collocated sample studies that were conducted by ARB in 1987. The results presented in Volume 2 are summarized and compared with the Bakersfield field study results in Chapter I of Volume 1. They provide complementary information on storage and transportation effects on TAC concentrations in Tedlar bags and stainless steel canisters.

CONCLUSIONS AND RECOMMENDATIONS

Major conclusions and recommendations as they relate to the five chapter topics are given below.

Chapter I - Storage and Transportation Effects

Storage and transportation effects on pollutant concentrations in Tedlar bags and stainless steel canisters were evaluated under both laboratory and field conditions. Bags show appreciable effects for almost all chemicals. The specific contaminants and level of contamination depended upon the storage conditions. Based on these results, we conclude that ARB's reported ambient concentrations from bag samples have been biased. For example, in the field study the average concentration of dichloromethane as reported by the automated gas chromatographic (AGC) system was 0.28 ppb. The initial bag concentration gave a similar value of 0.36 ppb. However, the final bag concentration after storage for several days was 3.36 ppb. This compares with the average ambient concentration of 2.3 ppb reported in ARB's 1985 Toxic Air Quality Data Summary. For illustrative purposes concentrations (ppb) of toluene and 1,1,1-trichloroethane are also shown:

	AGC	Bag Initial	Bag Final	ARB 1985 Ambient Data
toluene	5.52	5.18	17.18	7.9
1,1,1-trichloroethane	0.45	0.49	3.18	2.0

Three mechanisms of contamination were found to exist: permeation into bags, contamination from residual materials used in bag processing, and memory effects from previously filled bags.

In our laboratory studies no statistically significant storage and transportation effects were observed for canisters. However, the Bakersfield field study demonstrated statistically significant effects for several compounds. The canister effects were much smaller than for the bags, and except for freon-12 (23 percent increase) the effect was minimal (i.e. <10 percent). We also found that several of the "cleaned" canisters used for the field study were initially contaminated with several chlorinated hydrocarbons.

We recommend that ARB replace Tedlar bags with stainless steel canisters as soon as possible. In the mean time ARB should minimize the storage time of air samples collected with the Tedlar bags. We recommend that storage times not exceed 48 hours. Before converting to the canisters, the procedures for cleaning the canisters should be closely reviewed and documented.

Chapter II - Evaluation of Whole Air Sampling Devices

The commercial syringe and canister based sampling devices of interest to ARB were examined and shown to deliver reliable and valid samples to the analytical system. A certification process was developed to ensure that canister samplers are free of contamination. This process involves challenging the units with humidified zero air and humidified zero air spiked with known amounts of TACs. We recommend that this certification process be employed as an integral part of ARB's sampling and analysis program.

Chapter III - Evaluation of ARB's Analytical Method-ADDL002

Method ADDL002 provides a very suitable technique for determining ambient concentrations of most of the 17 target compounds. Freon-12, vinyl chloride, and freon-113 are not determined quantitatively by the method. A multi-adsorbent trap such as a Tenax/carbosieve S-II material is needed to obtain acceptable collection/recovery efficiencies of these three compounds.

Specified operating parameters for the gas chromatograph of flow rate, oven temperature programming rate and detector temperatures appeared to be set optimally for peak resolution. Precision levels were reproduced. No "carry-over" effects from previous samples or standards were observed.

The use of a 30 meter, OV-1, megabore, capillary column offered much improved resolution of the 17 target compounds compared to the packed column specified in Method ADDL002.

Oxygen doping of the carrier gas to the electron capture detector provided significantly enhanced peak area responses (100 to 200 fold) for the compounds, dichloromethane and 1,2-dichloroethane.

Chapter IV - Alternative Analytical Approaches

Modifications to the current analytical method were prioritized. We recommend that oxygen doping and multi-adsorbent trapping be incorporated into ARB's current methodology in the near future in order to improve present deficiencies of the method (i.e. low sensitivity and recovery of some species). The automation of the analytical system for bag/canister introduction and processing should also be actively pursued.

If ARB anticipates that their list of target compounds will expand, we recommend that they employ capillary columns for better peak resolving capability. We also recommend that ARB eventually switch to a mass spectrometric detector (selective ion monitoring mode) for their primary detection system.

Chapter V - Evaluation of ARB Quality Control Procedures

The broad range of quality control (QC) activities documented in ARB's QA manual, SOPs, and monthly QC reports demonstrate ARB's strong commitment to ensuring quality in the TAC sampling and measurement processes. In addition to the routine activities (such as duplicate analyses, daily control samples, multipoint calibrations, performance audits) ARB has conducted numerous special studies such as the "bag swap" and "bag/canister" studies to address additional quality issues.

Our investigation of ARB's QC program focussed primarily on the daily calibration activities and the quantitative techniques used to characterize the performance of the analytical methods. We also performed statistical analyses of selected ARB QC data to evaluate the accuracy, precision, and sensitivity of ARB's Method ADDL002.

Our conclusions and recommendations are:

- ARB's current method of linear regression and descriptive statistics on the multipoint calibration data to characterize the accuracy precision and sensitivity of their method is straightforward and gives good results. However, we recommend a more general statistical approach that will result in more realistic estimates of precision and will permit ARB to better characterize the performance of the analytical system.

- ARB's protocol for updating daily response factors is difficult to follow and may not cover all possible outcomes of the daily calibration and control samples analyses. Our statistical analysis of ARB supplied data demonstrated that

precision may be improved by simply updating the daily response factor each day. We recommend that ARB closely monitor the daily calibration and control sample data.

- ARB's selection of calibration and control sample concentrations is appropriate for most of the TACs being monitored. The only exceptions are the control sample concentrations for four of the target chemicals. Their concentrations are much higher than typical ambient levels.

- ARB's documentation of laboratory and field procedures contained in the QA manual, SOPs and monthly QC reports is quite detailed. However, the QA manual and the SOPs need to be updated to reflect changes that have been implemented in practice.

- We recommend that ARB develop a data management system to improve tracking the great volume of data.

- ARB should consider developing a set of data quality objectives (DQOs) as recommended by EPA's Quality Assurance Management Staff. DQOs are statements of the quality of data that must be achieved in various segments of a monitoring program. Only after the objectives are defined can the required amount and type of QC data be decided, and also what type of statistical procedures will be used to determine if the objectives are being met.

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CHAPTER I. LABORATORY STUDIES CONDUCTED BY BATTELLE

1.0 Introduction

The California Air Resources Board (CARB) measures toxic air contaminants (TACs) at numerous sites throughout the State using a procedure which employs Tedlar bags for sampling. The air samples are collected in Tedlar bags over a 24-h period, and then shipped to a central laboratory for analysis. The bags are transported to the laboratory by common carrier (van or bus), so the samples are stored in Tedlar bags for 1-2 days prior to analysis, and the storage conditions could be highly variable. Temperatures as high as 50°C have been reported in the compartments where bag samples are stored during transport, and it is likely that the samples are exposed to occasionally high levels of vehicle exhaust.

The purpose of the experiments reported in this section is to investigate the effect of permeation through the Tedlar film on the integrity of the TAC sample. A second objective is to determine whether or not "memory" effects can influence the measured TAC concentrations in Tedlar bags. Finally, a number of laboratory experiments were carried out to determine the storage capability of Tedlar bags and stainless steel canisters filled with Aadco zero air and with selected TACs at the 0.5 ppb level.

2.0 Tedlar Bag Permeation Studies

There have been several studies of air contaminant storage in Tedlar bags. Gordon et al.[1] described the use of Tedlar bags for low molecular weight hydrocarbon sampling in Los Angeles in 1968. Calvert,[2] in his analysis of LARPP data, pointed out potential problems with the stability of reactive pollutants during transport and storage in bags. Other problems that may affect the integrity of samples in bags include memory effects, contamination from the bag material, permeation of target chemicals into or out of the bag, degradation during storage and transport, and photochemical reactions in unprotected bags. In earlier studies with

Tedlar bags, we observed the release of large amounts of dimethyl acetamide from the Tedlar at elevated ambient temperatures. This material is present as a residue from the Tedlar manufacturing process,[3] and may reach concentrations of several ppmC in bags subjected to high ambient temperatures (~30°C). Seila et al.[4] have evaluated Tedlar as a container for hydrocarbon sampling and reported significant interference when the contents of the bag are exposed to sunlight. Polasek and Bullin[5] reported significant loss of organic compounds in Tedlar bags, whereas Kuntz[6] reported minimal loss of specific hydrocarbon species, but an overall gain in total organic concentration due to release of materials from the film. Arnts and Meeks[7] successfully used Tedlar bags for collection and storage of biogenic hydrocarbons, although they reported contamination of acetone and acetaldehyde. Knoll et al.[8] examined the storage stability of carbon tetrachloride, ethylene dichloride, tetrachloroethylene, and trichloroethylene in Tedlar bags. They reported significant stability problems for trichloroethylene and ethylene dichloride, even at high concentrations, and they developed a heat treatment to minimize memory effects, although residues of ethylene dichloride were not totally removed by this procedure. Lonneman et al.[9] reported that efforts to clean or condition Tedlar by heat treatment or solvent washing procedures were unsuccessful insofar as the use of Tedlar for smog chambers was concerned. Thrun et al.[10] examined several sampling containers, including Tedlar bags, for storage stability. At high concentrations, they reported excellent storage characteristics for ethane, propylene, methyl chloride, and benzene, but poor results for methanol and ethylene oxide.

This brief review indicates that the integrity of samples stored in Tedlar bags can be influenced by several factors, and is dependent on the nature of the stored compounds.

2.1 Integrity of TACs Stored in Tedlar Bags in Clean Environment

2.1.1. Objective. The objective of the laboratory experiments is to examine the loss of TACs from Tedlar bags by permeation through the Tedlar film. We studied permeation loss as a function of storage time, temperature, and relative humidity. A second objective of these experiments was to examine contamination of the samples due to 1) emissions from the

Tedlar film or 2) absorbed chemicals from prior samples (i.e. memory effects). The final objective was to investigate the effect of bag cleaning procedures on sample contamination.

2.1.2 Approach. Experiments have been carried out in two chambers shown schematically in Figure I-2.1. Tedlar sampling bags can be stored in these chambers under preselected conditions of temperature, humidity, and contamination levels. Experiments have been run with bags filled with ultra-clean air and with air spiked with 20 ppb levels of TACs. The bag contents were analyzed by an automated gas chromatograph (Hewlett Packard 5890) using dual flame ionization and electron capture detection. Samples were cryogenically concentrated prior to analysis. A valve and timer were used to control sampling from the bags to the chromatograph. Samples were transported through a 1/16 in. diameter stainless steel tube heated to 50°C. Individual sample lines connected each bag in a chamber to a manifold and valve, so the bags could be sampled and analyzed automatically while stored in the chambers.

Tedlar bags used in these experiments were supplied by the ARB. Bags from both the northern and southern ARB laboratories were used: northern lab bags were designated as N-(bag number) and bags from the southern lab as S-(bag number). Prior to each test, the bags were cleaned using the procedures employed by the respective laboratories. Ultra-clean air for bag cleaning, bag filling, and purging of the chambers was supplied by an Aadco, Inc. clean air generator.

Calibrations were performed by using a Columbia Scientific Inc. Model 1700 dynamic dilution system to generate several known concentrations of TACs by quantitative dilution. The source used for dynamic dilution was a cylinder containing known concentrations of 41 toxic air pollutants at nominal concentrations of 200 ppb per compound. The calibration cylinder is referenced to available NBS primary standards.

2.1.3 Results. The experiments reported in this section were conducted to investigate (1) permeation loss from Tedlar bags, (2) contamination/memory effects, and (3) cleaning effects. Results from these experiments are summarized below. In order to determine the significance of changes in concentration with time during the storage experiments, it was
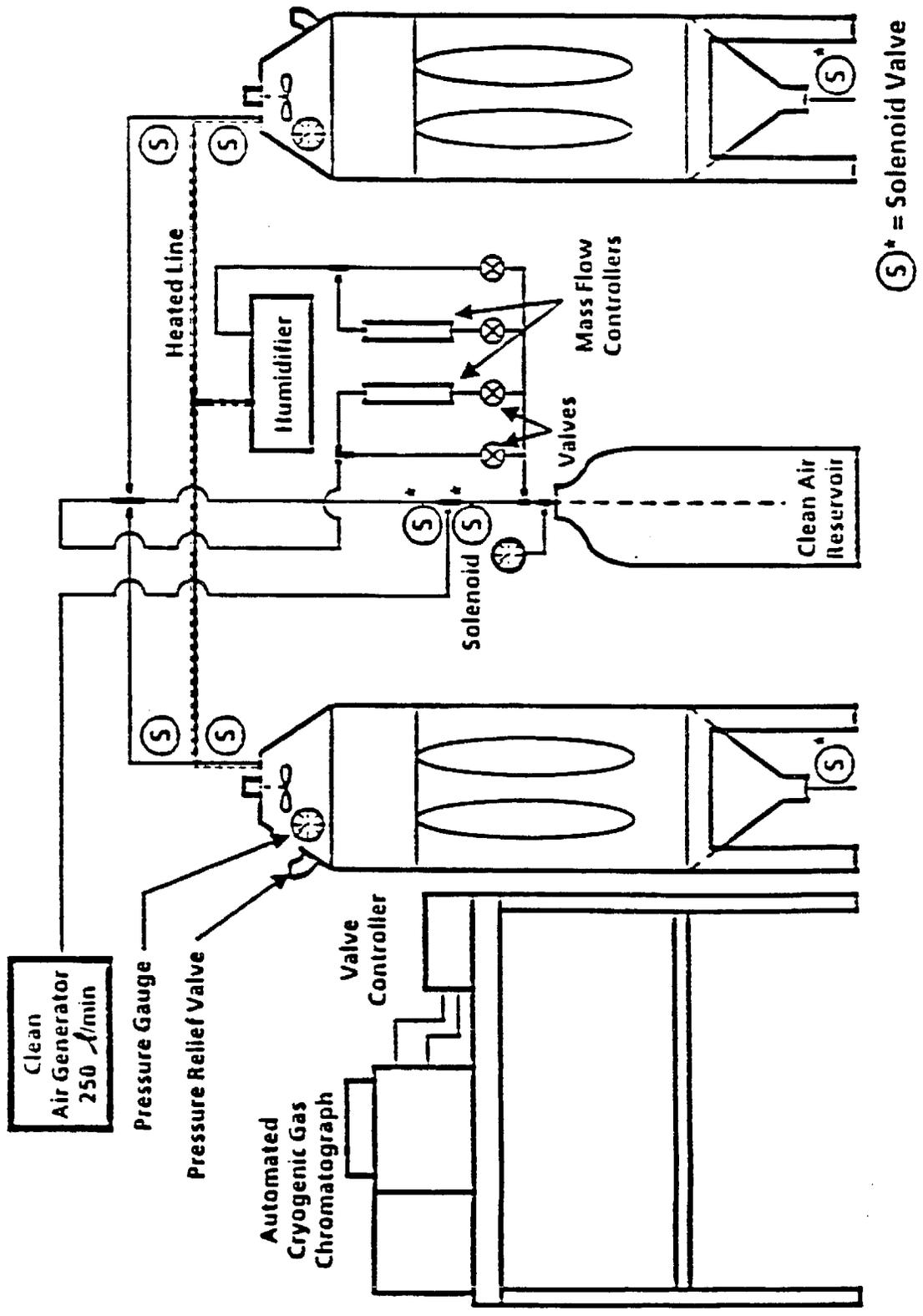
FIGURE I-2.1. SCHEMATIC DIAGRAM OF APPARATUS USED FOR TEDLAR BAG PERMEATION AND STORAGE STABILITY EXPERIMENTS

first necessary to establish the precision of the sampling/analysis methodology. Tests designed to characterize method precision are described below, followed by a discussion of the various storage experiments.

2.1.3.1 Measurement Precision. The precision tests involved making triplicate measurements of TACs in a test mixture on each of three separate days. The source of the organic species was a cylinder containing 200 ppb of each test compound. The cylinder contents were diluted dynamically to 10 ppb prior to sampling by the gas chromatograph. This procedure yielded a constant source of the test species over the multi-day precision experiments. Measurements were made on days 1, 2, and 4 of the experiments to cover the time scale of the Tedlar bag permeation experiments. Because the permeation experiments make use of flame ionization detector results, the precision tests focused on that detector.

A statistical analysis of the results from the precision experiments showed excellent precision both within a test day and between test days. With one exception, the overall relative standard deviation (RSD) for each of the target TACs was less than 3.2 percent. The overall RSD includes both between-day and within-day components of variation. With the same exception, the between-day variation (RSD) averaged 0.5 percent and was less than 1.3 percent for all TACs. The exception in both cases was dichlorodifluoromethane. This compound yields the lowest response by flame ionization (upon which these results are based), and the poorer precision for this substance is related to the small peak area obtained with the sample volumes used in this test. Even in this case, however, the between-day variation (RSD) was only 3.9 percent. The results for the other TACs indicate very good precision both within and between days, confirming our ability to detect concentration changes as low as a few percent per day for loss of TACs stored in Tedlar bags.

2.1.3.2 Permeation Loss of TACs During Storage in Tedlar Bags. Permeation of toxic air pollutants through Tedlar film has the potential to compromise the integrity of samples stored in Tedlar bags. Permeation depends on a concentration gradient across the membrane. Thus, if the concentration of a compound is higher in the bag than in the air surrounding the bag during storage, the compound could be depleted by

permeation <u>out</u> of the bag. Conversely, if the bag is stored in a contaminated area, toxic chemicals can permeate <u>into</u> the bag. Tests have been conducted to investigate both situations. The results of permeation inflow tests are reported in Section 2.2.

Tedlar bags from each ARB laboratory (N and S) were cleaned by the respective procedures and filled with ultra-clean air spiked with 10-20 ppb concentrations of 41 toxic pollutants. Table I-2.1 lists results for 17 TACs. Samples were stored in a clean environment for up to seven days at a temperature of either 25°C or 50°C. Tests were conducted with the bag and storage atmospheres at <10 percent humidity and at 50 percent humidity.

The results in Table I-2.1 are listed in terms of an average concentration change over a one day period. A negative loss rate indicates a concentration increase in the bag. In general, the results show very good stability at 25°C for chemicals stored in either northern or southern lab bags. Concentration changes averaged less than four percent per day for the 17 TACs. Relative humidity had no discernable effect on the change of concentration during storage. At 25°C, the concentration changes are of the same order as our measurement precision.

Storage experiments were carried out at 50°C to simulate the temperatures that have been measured in the bag storage compartments of vehicles used to transport bag samples from the field sites to the analysis laboratory. The results for storage at 50°C show generally low concentration variations over the period of a day, with the exception of toluene in the southern lab bag. The toluene concentration increased significantly during the storage period at an average rate of about 13 percent per day. Subsequent experiments examine the causes of this contamination.

The results from these experiments suggest that permeation loss of toxic chemicals at the ppb level from Tedlar bags is insignificant over a 1-2 day period compared to other sources of error. Toluene contamination was observed for one bag at high storage temperature. Contamination effects are discussed below.

2.1.3.3 Sample Contamination During Storage in Tedlar Bags. In the permeation experiments, as well as in other programs which utilized Tedlar bags for air sampling, we noted that significant contamination of

TABLE I-2.1.   TOXIC CHEMICAL LOSS FROM TEDLAR BAGS
DURING STORAGE IN CLEAN AIR

| | Average 24 hr Loss Rates (% per day) | | | |
| | 25°C | | 50°C | |
Compound	Northern Lab Bag	Southern Lab Bag	Northern Lab Bag	Southern Lab Bag
Dichlorodifluoromethane	.2	.1	1.6	.2
Vinyl Chloride	-1.5	.6	1.3	1.9
1,1-Dichloroethane	-1.7	.5	0	.6
Dichloromethane	-.8	3.7	1.6	3.4
1,1,2-Trichloro-1,2,2-Trifluoroethane	-1.2	--	0	.1
Trichloromethane	-.2	.6	-1.0	.3
1,2-Dichloroethane	-.2	2.0	-1.3	2.2
1,1,1-Trichloroethane	-1.2	.6	-1.6	-.1
Benzene	-.5	1.5	0	-.9
Carbon Tetrachloride	-.8	.7	-.3	.2
Trichloroethene	.2	2.1	.6	-.9
Toluene	-.5	2.6	2.3	-13.4
1,2-Dibromoethane	2.0	2.6	5.3	3.8
Tetrachloroethene	-1.2	1.8	-1.0	1.4
m&p-Xylene	1.5	2.7	2.3	2.7
o-Xylene	1.8	2.4	3.9	3.3

the sample occurred if the bag were heated. This effect is illustrated in Figure I-2.2. A Tedlar bag from the southern ARB laboratory was cleaned, filled with ultra-clean air, analyzed, and then stored at 25°C in clean air for 149 hours. The initial analysis showed only trace levels of organic constituents. Even after 149 hours of storage, the bag showed only a few trace contaminant peaks (see lower panel of Figure I-2.2). The bag was then stored in clean air at 50°C for 4.5 hours and reanalyzed. The results of this analysis are shown in the upper panel of Figure I-2.2. The chromatogram shows that the concentrations of a number of the constituents increased markedly after 4.5 hour storage at 50°C. A very large peak was observed at a retention time between 23 and 24 minutes, and significant increases occurred for peaks at 17.7 and 18.6 minutes.

In order to determine the nature of the contamination, a sample of air from this bag was analyzed using a GC with a mass selective detector (MSD) and data system. The GC/MSD identified the large contaminant peak at 23 minutes retention time as N,N-dimethylacetamide. Dimethylacetamide is present in Tedlar film as a residue from the manufacturing process, and has presented contamination problems in previous Tedlar bag air sampling programs. This contaminant peak does not interfere directly with the 17 TACs of concern to CARB. However, the very high concentrations of this compound, i.e. ppm levels, attained at elevated temperatures might possibly cause problems with TAC analysis by degrading GC column or detector performance, or by reacting (thermally or photochemically) to produce interfering compounds. Such effects have not been observed in our studies.

Other contaminant peaks with retention times shorter than dimethylacetamide were identified as ketones, carboxylic acids, and toluene. The observation of toluene contamination is especially significant because toluene is one of the 17 toxic compounds monitored by ARB. Toluene contamination of the Tedlar bag samples stored at 50°C was also observed during the permeation experiments discussed in Section 2.1.3.2.

Another set of storage experiments was carried out to investigate the effect of different storage temperatures. One bag from each ARB laboratory was cleaned at 25°C and another at 50°C. These four bags were filled with zero air and stored in zero air at 25 or 50°C for 149 hours. The results for the bags stored at 25°C are shown in Table I-2.2. Only three of the target compounds were observed in the sample air, and the

**Analysis of Zero Air in Tedlar Bag
After Storage for 4.5 h at 50°C**
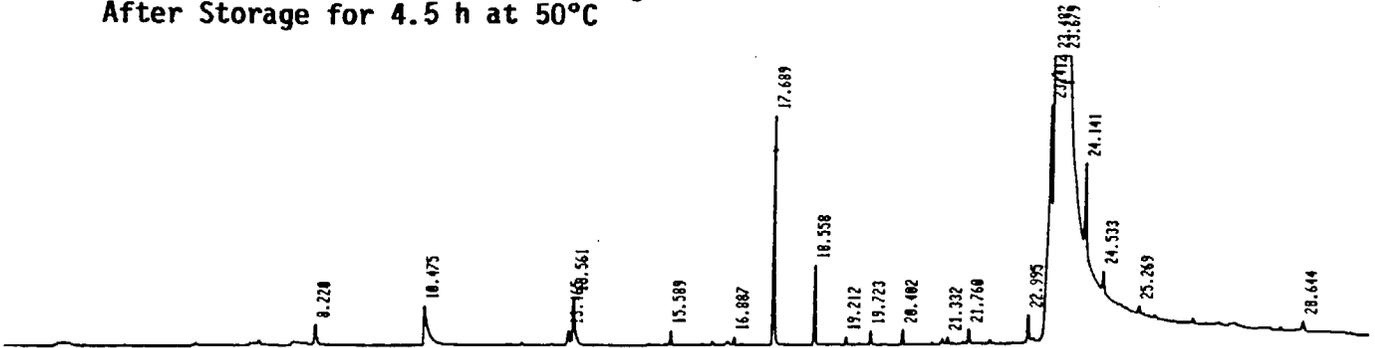
**Analysis of Zero Air in Tedlar Bag
After Storage for 149 h at 25°C**
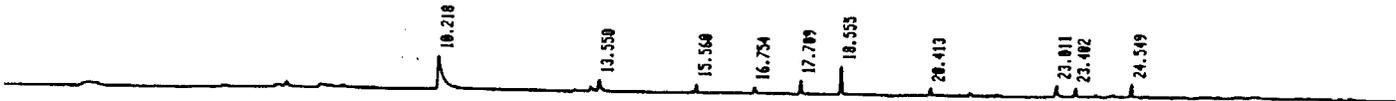
FIGURE I-2.2.   CHROMATOGRAMS OF ZERO AIR TEDLAR BAG AFTER
TWO STORAGE CONDITIONS

TABLE I-2.2. CONTAMINATION OF ZERO AIR BAGS*
STORED FOR 149 HOURS AT 25°C (ppb)

Compound	Bag S-4	Bag N-5
1,2 Dichloroethane	.09	.12
Toluene	.02	.13
Tetrachloroethene	.14	.33

* Bags cleaned at 25°C.

TABLE I-2.3. CONTAMINATION OF ZERO AIR BAGS*
STORED FOR 149 HOURS AT 50°C (ppb)

Compound	Bag S-6	Bag N-4
Dichloromethane	.65	1.2
Trichloromethane	0.0	.37
1,2-Dichloroethane	5.2	4.2
Toluene	6.9	68
Tetrachloroethene	1.8	1.6

* Cleaned at 50°C.

concentrations were less than 0.4 ppb. Results for the bags stored at 50°C are shown in Table I-2.3. The contaminants are more numerous and the concentrations are much higher following storage at 50°C. Toluene contamination was most serious, especially for bag N-4.

2.1.3.4 Memory Effects. An experiment was carried out to investigate Tedlar bag "memory" from previous samples. This experiment was carried out under extreme conditions of prior exposure to TACs and of temperature. A bag used for earlier permeation experiments at very high levels was cleaned by multiple purging and flushing with zero air for several hours at 50°C, and then filled with zero air. This bag was stored at 50°C in a chamber filled with zero air, and the bag contents were analyzed each hour for 24 hours. The outside of this bag had been exposed to ppm levels of TACs prior to this test, so the memory effect is expected to be greatly exaggerated compared to bags with a prior history of low level ambient air samples.

The data from this experiment are plotted in Figures I-2.3, I-2.4, and I-2.5. Eleven of the TACs showed substantial concentration increases over the 23 hour storage period. Several compounds showed elevated levels when the first sample was analyzed, which was less than one hour after filling the bag with zero air. These results suggest that significant memory effects occur for Tedlar bags stored at elevated temperatures. It must be emphasized that the very high contaminant concentrations observed in this experiment would not be anticipated for Tedlar bags used for ambient air sampling; the memory effects have no doubt been exaggerated by the high prior exposure levels. Nevertheless, these results demonstrate strongly that the potential for artificially high measurements is present, even for bags cleaned at 50°C.

2.2 Integrity of TAC Samples Stored in Contaminated Environment

2.2.1 Objective. The objective of the laboratory experiments described in this section is to investigate the integrity of TAC samples stored in Tedlar bags in contaminated environments. Experiments reported above showed that loss of TACs by permeation out of Tedlar bags is a slow process at typical ambient concentrations. However, permeation depends on
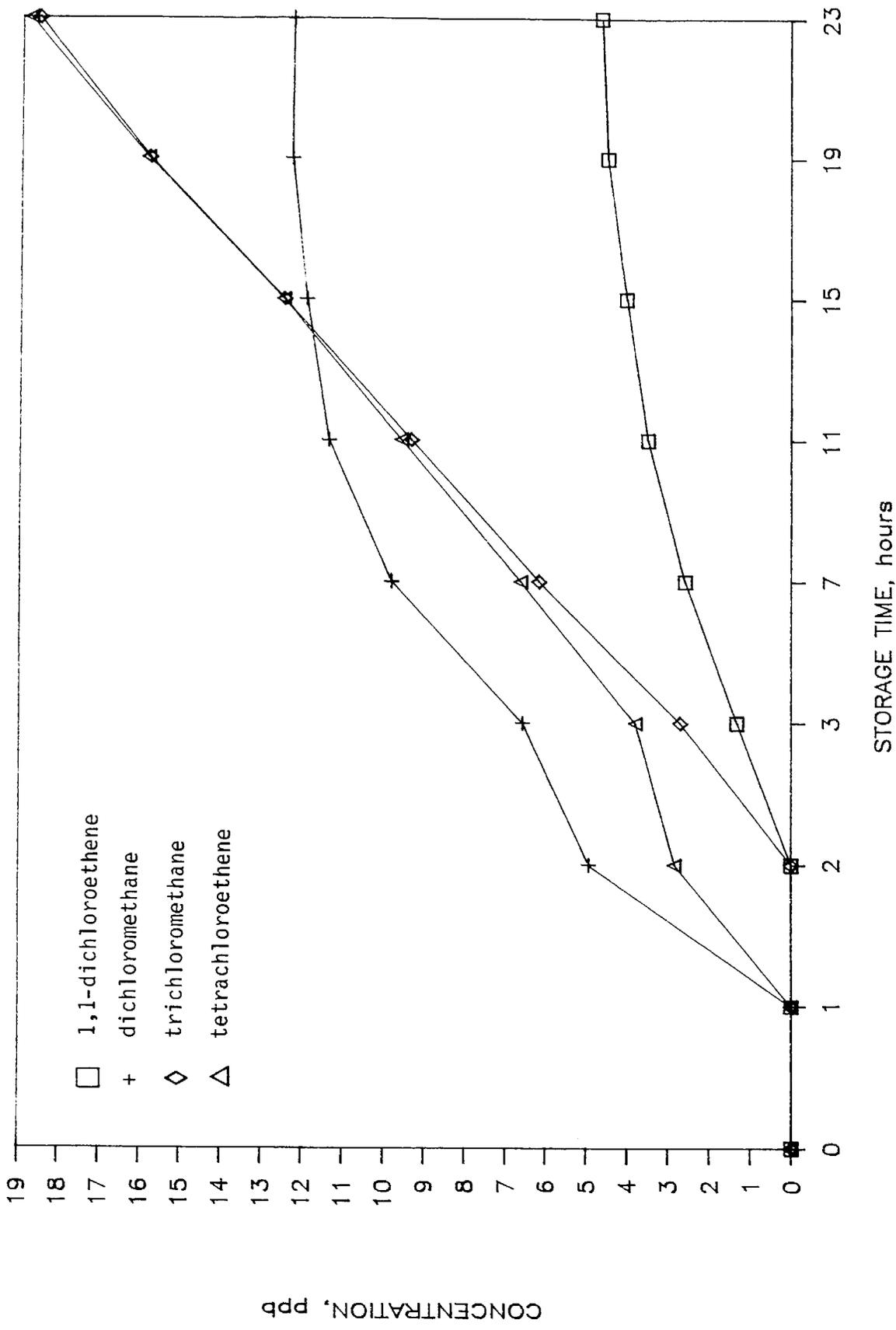
FIGURE I-2.3. TAC CONCENTRATIONS IN TEDLAR BAG STORED AT 50°C. BAG WAS PREVIOUSLY EXPOSED TO ppm CONCENTRATIONS OF TACs BEFORE CLEANING AT 50°C.
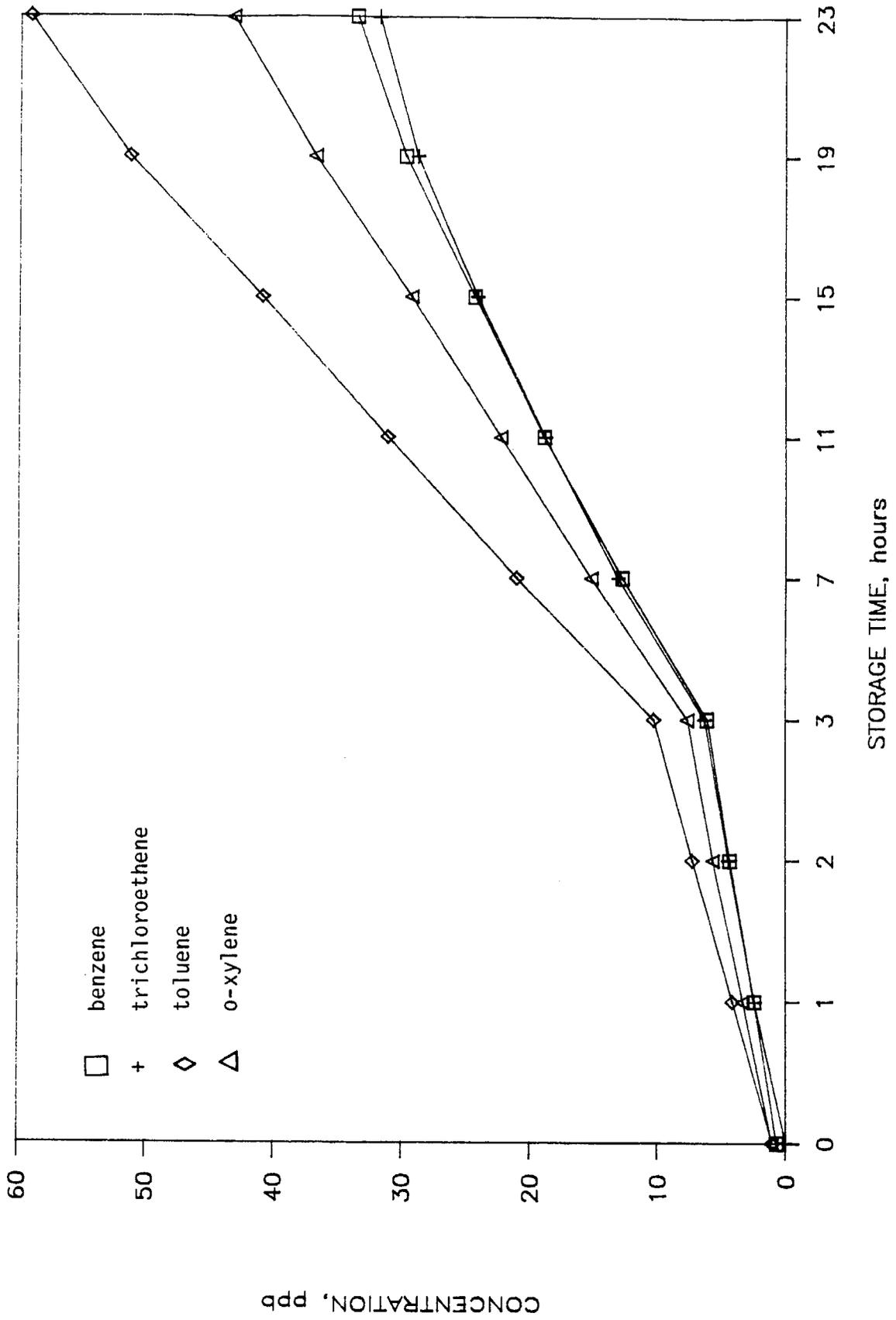
FIGURE I-2.4. TAC CONCENTRATIONS IN TEDLAR BAG STORED AT 50°C. BAG WAS PREVIOUSLY EXPOSED TO ppm CONCENTRATIONS OF TACs BEFORE CLEANING AT 50°C
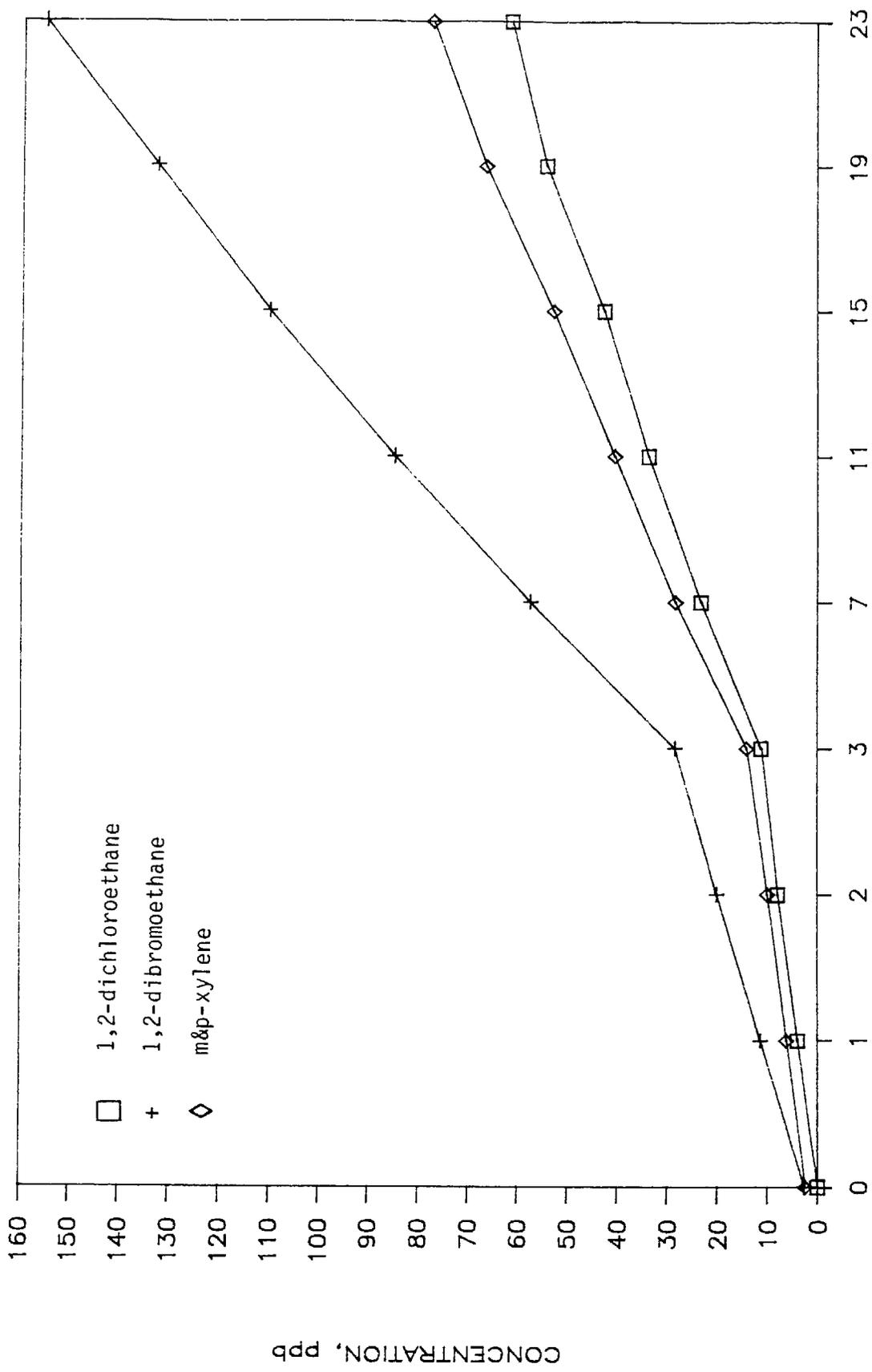
FIGURE I-2.5. TAC CONCENTRATIONS IN TEDLAR BAG STORED AT 50°C BAG WAS PREVIOUSLY EXPOSED TO ppm CONCENTRATIONS OF TACs BEFORE CLEANING AT 50°C

the concentration gradient across the membrane, so if samples are stored in highly contaminated areas, e.g. during transport to the laboratory, then permeation into the bag could seriously compromise the integrity of the sample. The experiments described in this section were requested by CARB to simulate a worst-case situation of storage in the cargo area of a transport vehicle in a hot environment contaminated with high levels of exhaust.

2.2.2 Approach. This experiment employed the heated chamber and automated sampling and analysis system described in Section 2.1.2. Four Tedlar bags, two each from the southern and the northern labs, were cleaned using the procedures employed by the respective laboratories. This involves room temperature flushing for the S bags and flushing at 50°C for the N bags. After cleaning, all four bags were filled with zero air at room temperature and one bag of each type was analyzed to be certain that the experiment was initiated with clean air. All four bags were placed in one chamber maintained at 50°C. This chamber was initially filled with zero air. Target chemicals were then injected into the chamber to obtain a design concentration of 10 ppm of each compound. A heated injector was used for syringe injection of 14 liquid TACs. Another gaseous TAC, dichlorodifluoromethane, was injected by gas-tight syringe. The four bags were analyzed by automated cryogenic gas chromatography at this time. The bags were stored under these conditions for the next nine days, and samples from each bag were analyzed on days 1, 2, 3, 4, 7, 8, and 9. A sample of the chamber atmosphere also was collected and analyzed on these days. Except for withdrawal of this daily sample, the chamber was sealed throughout the seven day period to preserve the highly contaminated storage condition. Calibrations were performed as noted in Section 2.1.2.

2.2.3 Results. The purpose of this experiment is to determine whether air samples stored in Tedlar bags under worst-case conditions will be contaminated by permeation of TACs into the bags. Bags containing clean air were stored in a severely contaminated atmosphere at 50°C for nine days, and the concentration changes in the bags were monitored over this period.

Results from these permeation inflow experiments are plotted in Figures I-2.6 and I-2.7 for two representative compounds, 1,1-dichloroethene and benzene. Most of the 15 TACs used in this experiment permeated through
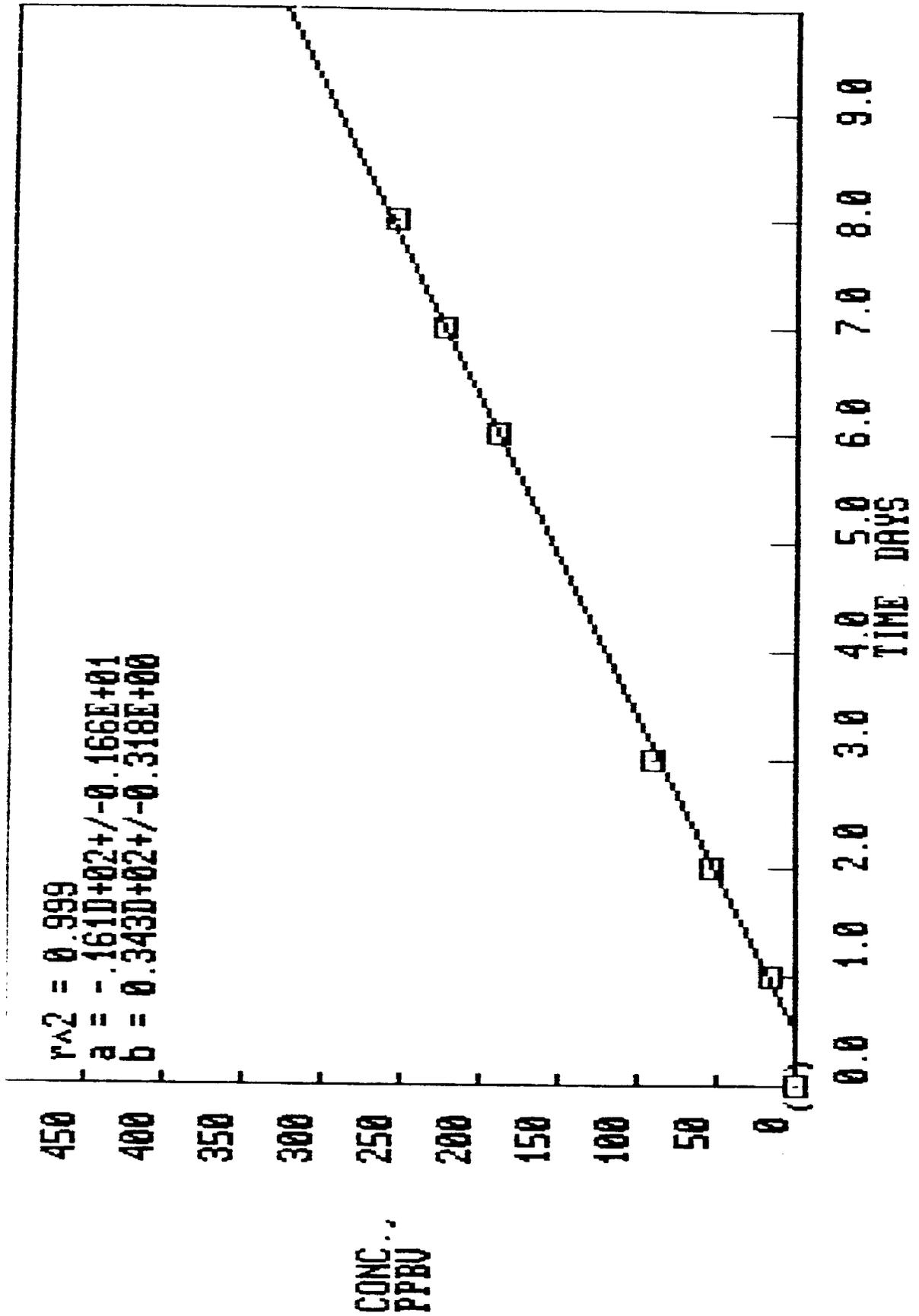
FIGURE I-2.6.   INCREASE IN 1,1-DICHLOROETHENE CONCENTRATION IN TEDLAR BAG

FIGURE I-2.7. INCREASE IN BENZENE CONCENTRATION IN TEDLAR BAG
STORED AT 50°C IN HIGHLY CONTAMINATED ATMOSPHERE

the Tedlar film within the first 48 hours of storage, and by the end of nine days of storage, the concentrations of most of the species were well above 100 ppb. The concentrations after two and nine days of storage are listed in Table I-2.4. These results demonstrate that Tedlar bag samples stored in contaminated areas run a serious risk of contamination due to permeation of TACs through the Tedlar film.

The data from this experiment can be used to calculate some permeation characteristics of the various TACs. The slopes and intercepts from the concentration vs time plots (e.g. Figures I-2.6 and I-2.7) have been used with the equations for diffusion in a plane sheet, developed in Crank[11], to calculate permeability constants and diffusion coefficients for these species. Table I-2.5 gives the values obtained for one of the Tedlar bags. The experiment was conducted at 50°C with a 5 mil (0.0127 cm) thick Tedlar bag having a surface area of 9,780 cm². Because this experiment was not designed to determine fundamental coefficients, the results should be viewed as order of magnitude estimates only.

2.3 Summary

These experiments demonstrate that permeation of TACs out of Tedlar bags is not a rapid process under normal conditions of temperature and TAC concentration. The permeation loss mechanism should not be important under most conditions. However, the results from Tedlar bag storage experiments show that serious contamination of samples collected in Tedlar bags can result from storage for extended periods, and especially if elevated temperatures (50°C) are encountered during storage. Three types of contamination were noted. One type involves residue from the manufacturing process, and can result in excessive levels of dimethylacetamide, ketones, and carboxylic acids. The second type of contamination involves a memory effect, i.e. retention on or in the Tedlar film of chemicals collected in previous samples, with subsequent release of these chemicals from the film at a later time. This type of contamination will depend on the prior history of the bag. The third type of contamination results from permeation of TACs into Tedlar bags during storage.

It is important to note that the storage experiments were carried out under extreme conditions. The length of the storage period and the

TABLE I-2.4. CONCENTRATIONS OF TACs IN CLEAN TEDLAR BAGS
STORED AT 50°C IN SEVERELY CONTAMINATED
ENVIRONMENTS FOR TWO AND NINE DAYS

Compound	Bag Concentration, ppb	
	2-Day Storage	9-Day Storage
1,1-Dichloroethene	15	255
Dichloromethane	165	1,648
Trichloromethane	2	310
1,2-Dichloroethane	15	1,038
Benzene	11	633
Trichloroethene	18	691
Toluene	4	744
1,2-Dibromomethane	8	1,495
Tetrachloroethene	3	169
m&p-Xylene	0	609
o-Xylene	2	198

TABLE I-2.5. QUANTITIES DERIVED FROM TEDLAR
BAG PERMEATION EXPERIMENTS

Compound	Temperature, °C	Permeability Constant[a]	Diffusion Coefficient, cm^2/s
1,1-Dichloroethene	50	1.9×10^{-5}	4.9×10^{-9}
Dichloromethane	50	4.3×10^{-5}	1.4×10^{-8}
Trichloromethane	50	2.3×10^{-5}	4.2×10^{-9}
1,2-Dichloroethane	50	3.7×10^{-5}	4.8×10^{-9}
1,1,1-Trichloroethane	50	1.7×10^{-5}	4.0×10^{-9}
Benzene	50	2.8×10^{-5}	4.9×10^{-9}
Carbon Tetrachloride	50	1.4×10^{-5}	4.1×10^{-9}
Trichloroethene	50	2.7×10^{-5}	5.3×10^{-9}
Toluene	50	2.8×10^{-5}	4.3×10^{-9}
1,2-Dibromoethane	50	4.2×10^{-5}	4.0×10^{-9}
Tetrachloroethene	50	1.3×10^{-5}	3.6×10^{-9}
m&p-Xylene	50	1.2×10^{-5}[b]	4.3×10^{-9}[b]
o-Xylene	50	1.1×10^{-5}	3.1×10^{-9}

(a) At 50°C; $P = \dfrac{\text{steady state flow rate (ppb/day) x thickness (cm)}}{\text{external concentration (ppm) x surface area (cm}^2)}$

(b) Result from a different bag.

elevated temperatures will not normally be encountered during ARB sampling. The bag memory effects also are atypical due to the high TAC doses encountered in the previous history of the sample bag. While the magnitudes of the effects observed are exaggerated due to the use of extreme conditions, the effects themselves are real and deserve attention, because they represent the potential for contamination of Tedlar bag samples. In subsequent sections of this report we discuss the results of storage studies carried out at realistic ambient concentrations.

3.0 Bag/Can Storage Studies

The Air Resources Board is particularly interested in determining if Summa polished stainless steel canisters would serve as improved replacements for Tedlar bags which are currently used by ARB. Battelle conducted two experiments in which the TAC concentrations in Tedlar bags and stainless steel canisters were monitored while the containers were stored under high temperatures for a period of seven days. In the first experiment, discussed in Section 3.1, the containers were filled with selected TACs at approximately the 0.5 ppb. level, representing a concentration that is within the ambient range for many of the target chemicals. The second experiment (Section 3.2) is similar to the first, except instead of filling the containers with TACs at the 0.5 ppb. level, they were cleaned and filled with zero air (Aadco Air) to evaluate contamination effects.

3.1 Storage of Bags and Canisters Filled
with 0.5 ppb TAC Concentrations

3.1.1 Objective. The objective of this laboratory experiments was to determine the storage capability of Tedlar bags and stainless steel canisters filled with selected TACs at the 0.5 ppb level. The ambient concentrations for these compounds typically range from below 0.05 ppb to more than 5 ppb. Thus, the level chosen for this experiment is within an order of magnitude of the typical ambient concentrations for each compound.

3.1.2 Approach. The sampling containers used for the storage tests included four Tedlar bags (2 each from ARB's Northern and Southern

laboratories) and four canisters (2 each from commercial vendors, SIS and BRC). In preparation for testing, the Tedlar bags underwent "cleaning" procedures as specified by each ARB laboratory. Canister cleaning involved initial flushing with zero air, followed by evacuation to <100 mtorr @ 50°C. All sampling containers were filled with Battelle's 41 component mixture at nominal concentrations of 0.5 ppb. A dynamic dilution manifold equipped with humidified zero air was employed to facilitate the filling procedure. During the testing period, the sampling containers were stored in an environmental chamber at 50°C to simulate worst case temperature/storage conditions. Room air was directed through the chamber during this time period. All sampling containers were analyzed after 1, 3, and 6 days of storage. The above tests were repeated using zero air as the target mixture (Aadco air).

During the preliminary experiments a modification to the GC/MSD was completed that allowed us to automate the analysis of all sampling containers. As a result, calibration runs and all eight samples could be easily analyzed within the same day. Prior to this change, only 6 samples could be processed per day. Thus this improvement provided a much better means for comparing canister and bag results. Table I-3.1 shows the test runs that were completed.

3.1.3 Results. Data obtained from the experimental program consist of measured concentrations of 41 chemicals contained in 8 sampling devices stored at 50 degrees C for 7 days. A gas mixture containing target concentrations of approximately 0.5 ppb. was used to fill the devices at the beginning of the storage period. Chemical concentrations measured by automated gas chromatography were obtained from each device on days 2, 4, and 7. The eight sampling devices are denoted by

- NLB Tedlar Bags (BN1 and BN2),
- SLB Tedlar Bags (BS1 and BS2),
- BRC Canisters (CB1 and CB2), and
- SIS Canisters (CS1 and CS2).

Response factors were computed from daily QC analyses performed before and after the analyses of the 8 stored samples on each measurement

TABLE I-3.1. TEST RUNS COMPLETED TO DETERMINE SAMPLE
STORAGE CHARACTERISTICS OF VARIOUS SAMPLING
DEVICES (TASK 2 LABORATORY EXPERIMENTS)

Sampling Device[a]	Test Day[b]			
	1	2	4	7
BN1	F	A	A	A
BN2	F	A	A	A
BS1	F	A	A	A
BS2	F	A	A	A
CS1	F	A	A	A
CS2	F	A	A	A
CB1	F	A	A	A
CB2	F	A	A	A

(a) BN and BS refer to Tedlar bags from the
Northern and Southern Laboratories. CS and CB
refer to canisters from SIS and BRC.

(b) F = Fill sampling device at ~0.5 ppb.
A = Analyze sample with automated GC/MSD
system.

day. The same calibration standard used to fill the devices on day 1 was used to determine the response factors. Although the daily response factors can be used to compensate for instrument changes between days, our precision analysis demonstrated that for most chemicals there was no evidence of day-to-day instrument variability. Thus the average response factor was used to quantitate chemical concentrations. Further discussion of this approach is presented in Section 3.1.4.

A preliminary analysis using linear regression analysis demonstrated that there was no significant change in any of the chemical concentrations for samples stored in canisters. We did find a few chemicals that demonstrated a statistically significant trend (at the 0.05 level of significance). However, in these cases the maximum concentration change during the 7 day study was less than 0.05 ppb. (approximately 10% of the fill concentration). Furthermore, as discussed in Section 3.1.4, the relative standard deviation of the analytical method is less than 10% for each of the chemicals.

The regression analysis also demonstrated that there were several statistically significant changes in chemical concentrations for samples stored in Tedlar bags. The most obvious change was a 75 to 85 ppb net increase in benzene over the 7 day storage study. These results are illustrated in Figure I-3.1.

After the preliminary analysis demonstrated that there was no significant change in chemical concentrations in samples stored in canisters, we used a more accurate and precise method of quantitating concentrations in Tedlar bag samples. Instead of calculating a response factor based on daily QC samples we combined the data collected from the daily canister analyses to compute the relative response factor

$$RF_C = PA_C/C_t,$$

where PA_C is the average GC peak area from the 4 daily canister analyses and C_t is the target concentration (ppb) of the sample used to fill the devices. The measured concentration for an individual bag on each analysis day was computed by

$$C_B = PA_B/RF_C.$$

#=17 Compound Name=benzene Target Concentration (ppb)=0.54
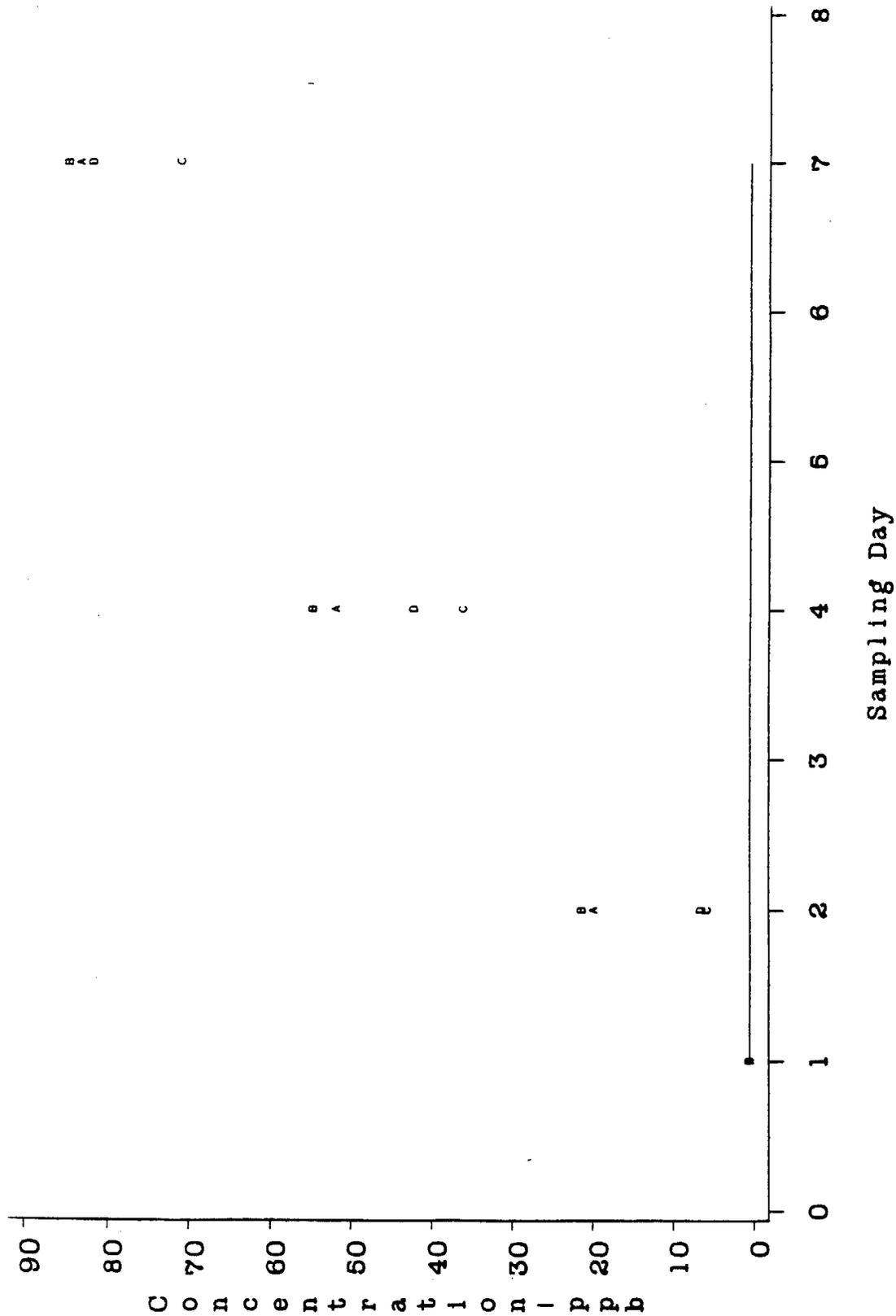
FIGURE I-3.1. THE LARGEST STORAGE EFFECT WAS THE INCREASE IN BENZENE CONCENTRATION

There are several reasons for estimating bag concentrations in this way. First of all we demonstrated with the regression analysis that there were no significant changes in concentrations in the canister samples. Secondly, the canisters contain humidified air, the same as the bags. Finally, using the average of 4 canister analyses to calculate a daily response factor, we eliminate day-to-day instrument effects that exist for certain chemicals, while introducing only minimal additional variation for those that are not affected by day-to-day effects.

Tables I-3.2 and I-3.3 summarize the experimental results for NLB and SLB bag samples, respectively. The tables contain the average concentration of ARB selected chemicals in the bag samples on days 2, 4, and 7. Also presented are the absolute and percentage changes in chemical concentrations over the 7 day storage study. The chemicals that had a statistically significant change (determined by linear regression analysis) are designated with an asterisk (*). Notice that nearly the same set of chemicals were identified for the NLB and SLB bags. Only the NLB bag results for 1,2-dichloroethane and 1,1,1-trichloroethane were statistically inconclusive. For some chemicals the magnitude of the change depended on the source of the bags. The most significant difference between NLB and SLB bags is the level of toluene contamination. NLB bags had a net increase of 1.07 ppb., while the SLB bags had a net increase of 8.55. The largest and most significant increase was the level of benzene (77 - 85 ppb).

Other chemicals increasing in concentrations include dichloromethane (0.52 - 0.66 ppb.), m+p-xylene (0.45 - 0.63 ppb.), o-xylene (0.11 - 0.25 ppb.), and styrene (0.15 - 0.37 ppb.). The concentration of several chemicals decreased by 0.1 to 0.26 ppb. (20 to 50 percent) during the 7 day study. One possible explanation is that certain chemicals tend to adhere to the walls of the bags. This might account for the relatively low concentrations of 1,2-dichloroethane and 1,2 -dibromoethane typically found in ambient samples by ARB.

Plots of the measured concentrations versus storage day for each of the 4 bag samples are presented in Appendix I-A.

3.1.4 Precision Analysis. In order to determine whether or not the storage effects observed were statistically significant we performed a

TABLE I-3.2.   TAC BAG CONCENTRATION DETERMINED BY COMPARISON
              WITH CANISTERS (ppb) NLB BAGS

#	Compound	Target ppb	Average Concentration (ppb)				
			Day 2	Day 4	Day 7	Δ(7-1)	(%)
1	Dichlorodiflouromethane (Freon-12)	0.49	.	0.48	0.49	0.00	0.07
4	Vinyl Chloride	0.88	0.92	0.85	0.87	-0.01	-0.81
8	1,1-Dichloroethene	0.61	0.61	0.63	0.61	-0.00	-0.10
9	Dichloromethane (DCM)	0.78	0.89	1.03	1.30	0.52	66.91*
11	1,1,2-Trichloro-1,2,2-Trifluoroethane	0.52	0.49	0.49	0.47	-0.05	-9.07
14	Trichloromethane (CHCL3)	0.66	0.63	0.64	0.65	-0.01	-1.29
15	1,2-Dichloroethane (EDC)	0.64	0.58	0.58	0.53	-0.11	-17.58
16	1,1,1-Trichloroethane (TCEA)	0.51	0.52	0.59	0.61	0.10	19.36
17	Benzene	0.54	20.66	53.65	85.08	84.54	15656.05*
18	Carbon Tetrachloride (CCL4)	0.56	0.57	0.56	0.54	-0.02	-3.33
20	Trichloroethene (TCE)	0.56	0.55	0.57	0.60	0.04	7.80
24	Toluene	0.47	0.96	1.37	1.54	1.07	226.67*
25	1,2-Dibromoethane (EDB)	0.58	0.52	0.42	0.35	-0.23	-39.24*
26	Tetrachloroethene (PERC)	0.66	0.66	0.66	0.66	0.00	0.34
29	m+p-Xylene	0.41	0.68	0.51	0.86	0.45	109.82*
30	Styrene	0.43	0.77	0.89	0.80	0.37	86.54*
32	o-Xylene	0.41	0.49	0.62	0.66	0.25	61.56*
37	m-Dichlorobenzene	0.41	0.28	0.22	0.16	-0.25	-61.12*
38	p-Dichlorobenzene	0.34	0.26	0.23	0.16	-0.18	-51.71*
39	o-Dichlorobenzene	0.41	0.27	0.21	0.15	-0.26	-63.47*

* Estimates of Δ are larger than 0.05 and statistically significant.

TABLE I-3.3. TAC BAG CONCENTRATION DETERMINED BY COMPARISON
WITH CANISTERS (ppb) SLB BAGS

#	Compound	Target ppb	Average Concentration				
			Day 2	Day 4	Day 7	$\Delta(7-1)$	(%)
1	Dichlorodiflouromethane (Freon-12)	0.49	0.52	0.54	0.48	-0.01	-2.79
4	Vinyl Chloride	0.88	0.88	0.84	0.82	-0.06	-6.99
8	1,1-Dichloroethene	0.61	0.59	0.60	0.57	-0.04	-6.16
9	Dichloromethane (DCM)	0.78	0.95	1.12	1.44	0.66	85.01*
11	1,1,2-Trichloro-1,2,2-Trifluoroethane	0.52	0.49	0.51	0.53	-0.01	-10.54
14	Trichloromethane (CHCL3)	0.66	0.62	0.64	0.63	-0.03	-3.83
15	1,2-Dichloroethane (EDC)	0.64	0.60	0.58	0.54	-0.10	-15.51*
16	1,1,1-Trichloroethane (TCEA)	0.51	0.52	0.55	0.58	0.07	12.91*
17	Benzene	0.54	6.20	39.46	77.36	76.82	14225.84*
18	Carbon Tetrachloride (CCL4)	0.56	0.55	0.56	0.55	-0.01	-2.58
20	Trichloroethene (TCE)	0.56	0.54	0.56	0.56	-0.00	-0.34
24	Toluene	0.47	7.34	9.31	9.02	8.55	1818.16*
25	1,2-Dibromoethane (EDB)	0.58	0.49	0.42	0.32	-0.26	-45.30*
26	Tetrachloroethene (PERC)	0.66	0.67	0.67	0.65	-0.01	-0.90
29	m+p-Xylene	0.41	0.67	0.90	1.04	0.63	154.09*
30	Styrene	0.43	0.62	0.65	0.58	0.15	33.87*
32	o-Xylene	0.41	0.45	0.49	0.52	0.11	25.72*
37	m-Dichlorobenzene	0.41	0.29	0.22	0.16	-0.25	-60.66*
38	p-Dichlorobenzene	0.34	0.25	0.19	0.14	-0.20	-57.60*
39	o-Dichlorobenzene	0.41	0.27	0.21	0.15	-0.26	-64.38*

* Estimates of Δ are larger than 0.05 and statistically significant.

precision analysis using the QC data generated on each day of the study. Three QC analysis were performed on day 1 during the fill operation and 2 QC analyses each were performed on days 2, 4, and 7. However, one of the analyses on day 4 had to be discarded. The day 1 analyses were performed on humidified samples, while the others were performed on dry samples.

Our study of these data demonstrate that the automated GC has a relative standard deviation of between 5% and 9%. Estimates of the relative standard deviations for the original 16 target chemicals are provided in Table I-3.4. Although we provide test results for a total of 20 target chemicals, including four additional chemicals requested by ARB, we did not believe that it was necessary to perform the precision analysis for the four additional chemicals.

Statistical variance component analysis was used to estimate within-day and between-day variance components. We used the statistical models

$$RF1 = \mu_h + \epsilon_w,$$

and

$$RF = \mu_d + \epsilon_w + \epsilon_b,$$

where

RF1 is a response factor on day 1,
RF is a response factor on day 2, 4, or 7,
μ_h is the mean RF for a humidified sample,
μ_d is the mean RF for a dry sample,
ϵ_w is a random error for within day effects, and
ϵ_b is a random error for between day effects.

The relative standard deviations of the random error terms are

$$RSD_w = \sigma_w/\mu,$$

and

$$RSD_b = \sigma_b/\mu,$$

where σ_w and σ_b are the absolute standard deviations of the within-day and between-day effects, respectively, and μ is the mean response factor. The total relative standard deviation of a measurement is given by

TABLE I-3.4. PRECISION ANALYSIS FOR TASK 2 STUDY

#	Compound(6)	$\overline{RF}$(1)	$\overline{RF}$(2)	RSD(%)	$\overline{RF/RF1}$
1	Dichlorodiflouromethane	14603	14434	5.04	0.99
4	Vinyl Chloride	4710	4387	8.34(3)	0.93
8	1,1-Dichloroethene	4299	4357	9.38(3)	1.01
9	Dichloromethane	4082	3814	6.02	0.93
11	1,1,2-Trichloro-1,2,2-Trifluoroethane	10575	11846	8.51	1.12
14	Trichloromethane	10154	9592	7.35	0.94
15	1,2-Dichloroethane	7859	7613	7.41	0.97
16	1,1,1-Trichloroethane	7059	7347	8.09	1.04
17	Benzene	14312	13669	8.26(3)	0.96
18	Carbon Tetrachloride	9680	9626	8.69(3)	0.99
20	Trichloroethene	6967	6584	8.22	0.95(4)
24	Toluene	19290	16697	7.36	0.87(4)
25	1,2-Dibromoethane	11299	10433	9.24	0.92
26	Tetrachloroethene	8588(5)	7847	6.54	0.91(4)
29	m+p-Xylene	20913(5)	16562	9.05	0.79(4)
32	o-Xylene	19015	16432	9.50	0.86

(1) Average RF for day 1 - humidified samples.
(2) Average RF for days 2, 4, and 7 - dry samples.
(3) Significant between day variation was detected.
(4) Significantly different from 1.0.
(5) Outliers removed.
(6) Precision estimates were not calculated for compounds 30, 37, 38, and 39. They were not among the original target compounds.

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$$RSD^2 = RSD_w^2 + RSD_b^2.$$

Besides estimating the precision of the method we performed two statistical tests to determine if there were significant between-day effects. A statistical F-test was used to determine if there was a significant between-day variance component. We did find a significant effect for two chemicals, as shown in Table I-3.4. However, in these cases the effect is not very large. The RSDs in Table I-3.4 reflect the total variation due to both random effects.

We also used these data to determine if there was a significant difference between the analyses of humidified and dry samples. That is, we tested to see if $\mu_h = \mu_d$. The results of a t-test are shown in Table I-3.4.

The precision analysis helped us to identify statistical outliers in the data, select an appropriate method of quantitation, and determine which effects are statistically significant. Because we found some evidence of between-day effects and a small difference between the analyses of dry and humidified samples for some chemicals we elected to use the canister data to quantitate the bag sample results. Finally, the precision analysis gave us a statistical basis for evaluating the storage effects. Since the results presented in Tables I-3.2 and I-3.3 represent the average of 2 bag sample concentration estimates, we can say with approximately 95 percent confidence that if there is no storage effect the net change (percent) in concentration on any day should be no greater than

$$2 \cdot RSD/\sqrt{2}.$$

Using a conservative value of 10% for the RSDs, we should expect no more than a 14% or 0.07 ppb. change in estimated concentrations after day 1.

3.2 Storage of Bags and Canisters Filled with Zero Air

This was the second experiment involving the monitoring of TAC concentrations in Tedlar bags and stainless steel canisters stored under high temperatures for a period of seven days. However, instead of filling the containers with typical ambient concentrations of TACs, this experiment

was performed with clean containers filled with zero air to test for contamination effects.

3.2.1 Objective.

The objective of this laboratory experiment was to determine if there are significant contamination effects of storing samples in Tedlar bags and stainless steel canisters at elevated temperatures.

3.2.2 Approach.

Data obtained from the zero air storage study consist of measured concentrations of 41 chemicals contained in 8 sampling devices stored at 50 degrees C for 7 days. Zero air (Aadco Inc.) was used to fill the devices at the beginning of the storage period. Chemical concentrations measured by automated gas chromatography were obtained from each device on days 2, 4, and 7. This experiment replicates the previous bag/can storage experiment in which we used target concentrations of approximately 0.5 ppb. (See Section 3.1)

The 8 sampling devices are denoted by

- NLB Tedlar Bags (BN1 and BN2),

- SLB Tedlar Bags (BS1 and BS2),

- BRC Canisters (CB1 and CB2), and

- SIS Canisters (CS1 and CS2).

Response factors were calculated from daily QC analyses performed before and after the analysis of the eight stored samples on each measurement day. The same calibration standard was also analyzed three times during the fill operation on day 1.

Preliminary evaluation of the data revealed several potential outliers in the data. There were unusually high levels of five chemicals on each day for the second Tedlar bag from the Northern Lab (BN2). The chemicals which had abnormally high levels are: 1,1,1-trichloroethane, toluene, tetrachloroethane, m+p-xylene, and o-xylene. Although it is not clear why the levels of these chemicals were so much higher than those observed in the other three bags, we removed these data from the subsequent analyses. Removing the potential outliers does not affect the statistical

significance of the concentration changes but it does result in more conservative estimates of the changes for the NLB bags.

Tables I-3.5 through I-3.8 summarize the experimental results for the 4 types of sample containers. Each table contains the average concentration of ARB selected chemicals in the bag or can samples on days 2, 4, and 7. Also presented are the average concentrations measured during the fill operation on day 1 and the absolute changes in chemical concentrations over the 7-day storage study. Notice that some chemicals were found at trace levels during the fill operation.

In Tables I-3.5 and I-3.6, the absolute concentration changes from the 0.5 ppb storage study are also presented. The chemicals that had a statistically significant change (determined by linear regression analysis) are designated with an asterisk (*). Just as in the 0.5 ppb storage study, no significant changes in chemical concentrations were found in the canister samples. However, for the NLB and SLB bag samples, nearly the same set of chemicals were identified as having significant changes. Only the SLB bag result for 1,1,1-trichloroethane was statistically inconclusive. Also, nearly the same set of chemicals in the NLB and SLB bags that demonstrated significant changes in the previous study were also significant in this study.

Chemicals whose concentration increased in the bag samples include

- dichloromethane (0.63-0.67 ppb),

- 1,1,1-trichloroethane (0.13 ppb),

- benzene (14-20 ppb),

- trichloroethene (0.08 ppb),

- toluene (0.42-0.95 ppb),

- tetrachloroethane (0.06 ppb),

- m+p-xylene (0.46-0.47 ppb),

- styrene (0.19-0.85 ppb),

- o-xylene (0.18 ppb), and

- m-, p-, and o-dichlorobenzene (0.02-0.09 ppb).

TABLE I-3.5. TAC CONCENTRATIONS FOR ZERO AIR STORAGE STUDY - NLB BAGS

#	Compound	Fill ppb	Average Concentration (ppb)			Δ(7-1)a	Δ(0.5)b
			Day 2	Day 4	Day 7		
1	Dichlorodiflouromethane (Freon-12)	0.01	NDc	ND	ND	-0.01	
4	Vinyl Chloride	0.00	ND	ND	ND	0.00	
8	1,1-Dichloroethene	ND	ND	ND	ND	----	
9	Dichloromethane (DCM)	ND	0.24	0.48	0.67	0.67*	(0.52)
11	1,1,2-Trichloro-1,2,2-Trifluoroethane	0.05	0.05	0.03	0.03	-0.02	
14	Trichloromethane (CHCL3)	ND	0.02	0.03	0.05	0.05	
15	1,2-Dichloroethane (EDC)	ND	ND	0.00	0.01	0.01	
16	1,1,1-Trichloroethane (TCEA)	0.03	0.08	0.12	0.17	0.13*	
17	Benzene	0.02	1.75	5.26	13.94	13.92*	(84.54)
18	Carbon Tetrachloride (CCL4)	ND	ND	ND	ND	----	
20	Trichloroethene (TCE)	ND	ND	0.05	0.08	0.08*	
24	Toluene	0.04	0.22	0.35	0.46	0.42*	(1.07)
25	1,2-Dibromoethane (EDB)	ND	ND	ND	ND	----	(-0.23)
26	Tetrachloroethene (PERC)	ND	0.03	0.04	0.06	0.06*	
29	m+p-Xylene	0.02	0.09	0.37	0.48	0.46*	(0.45)
30	Styrene	0.00	1.10	1.06	0.85	0.85*	(0.37)
32	o-Xylene	0.00	0.09	0.14	0.19	0.18*	(0.25)
37	m-Dichlorobenzene	0.01	0.02	0.02	0.04	0.02*	(-0.25)
38	p-Dichlorobenzene	0.01	0.11	0.11	0.10	0.09*	(-0.18)
39	o-Dichlorobenzene	0.01	0.03	0.03	0.04	0.03*	(-0.26)

* Estimates of Δ are larger than 0.05 and statistically significant.
(a) Δ(7-1) is the concentration change between day 1 and day 7.
(b) Δ(0.5) is the statistically significant (0.05 level) change observed in the 0.5 ppb storage study.
(c) ND = Not Detected.

TABLE I-3.6. TAC CONCENTRATIONS FOR ZERO AIR STORAGE STUDY - SLB BAGS

#	Compound	Fill ppb	Average Concentration (ppb)				
			Day 2	Day 4	Day 7	Δ(7-1)a	Δ(0.5)b
1	Dichlorodiflouromethane (Freon-12)	0.01	NDc	ND	ND	- 0.01	
4	Vinyl Chloride	0.00	ND	ND	ND	- 0.00	
8	1,1-Dichloroethene	ND	ND	ND	ND	----	
9	Dichloromethane (DCM)	ND	0.23	0.45	0.63	0.63*	(0.66)
11	1,1,2-Trichloro-1,2,2-Trifluoroethane	0.05	0.05	0.07	0.05	-0.00	
14	Trichloromethane (CHCL3)	ND	0.03	0.03	0.04	0.04	
15	1,2-Dichloroethane (EDC)	ND	0.02	0.02	0.03	0.03	(-0.10)
16	1,1,1-Trichloroethane (TCEA)	0.03	0.04	0.06	0.08	0.05	(0.07)
17	Benzene	0.02	8.70	12.99	20.23	20.21*	(76.82)
18	Carbon Tetrachloride (CCL4)	ND	ND	ND	ND	----	
20	Trichloroethene (TCE)	ND	0.02	0.04	0.08	0.08*	(8.55)
24	Toluene	0.04	0.66	0.88	0.99	0.95*	(-0.26)
25	1,2-Dibromoethane (EDB)	ND	0.05	0.05	0.05	0.05	
26	Tetrachloroethene (PERC)	ND	0.04	0.06	0.06	0.06*	
29	m+p-Xylene	0.02	0.19	0.36	0.48	0.47*	(0.63)
30	Styrene	0.00	0.17	0.21	0.19	0.19*	(0.15)
32	o-Xylene	0.00	0.10	0.15	0.19	0.18*	(0.11)
37	m-Dichlorobenzene	0.01	0.06	0.07	0.07	0.06*	(-0.25)
38	p-Dichlorobenzene	0.01	0.07	0.07	0.07	0.06*	(-0.20)
39	o-Dichlorobenzene	0.01	0.07	0.07	0.07	0.06*	(-0.26)

* Estimates of Δ are larger than 0.05 and statistically significant.
(a) Δ(7-1) is the concentration change between day 1 and day 7.
(b) Δ(0.5) is the statistically significant (0.05 level) change observed in the 0.5 ppb storage study.
(c) ND = Not Detected.

TABLE I-3.7 TAC CONCENTRATIONS FOR ZERO AIR STORAGE STUDY - BRC CANISTERS

#	Compound	Fill ppb	Average Concentration (ppb)			
			Day 2	Day 4	Day 7	Δ(7-1)a
1	Dichlorodiflouromethane (Freon-12)	0.01	0.02	0.02	0.00	-0.01
4	Vinyl Chloride	0.00	NDb	ND	ND	-0.01
8	1,1-Dichloroethene	ND	ND	ND	ND	---
9	Dichloromethane (DCM)	ND	ND	ND	ND	---
11	1,1,2-Trichloro-1,2,2-Trifluoroethane	0.05	0.04	0.05	0.03	-0.02
14	Trichloromethane (CHCL3)	ND	ND	0.00	0.01	0.01
15	1,2-Dichloroethane (EDC)	ND	ND	ND	ND	---
16	1,1,1-Trichloroethane (TCEA)	0.03	0.05	0.06	0.04	0.00
17	Benzene	0.02	0.02	0.04	0.04	0.02
18	Carbon Tetrachloride (CCL4)	ND	ND	ND	ND	---
20	Trichloroethene (TCE)	ND	ND	ND	ND	---
24	Toluene	0.04	0.03	0.05	0.07	0.03
25	1,2-Dibromoethane (EDB)	ND	ND	ND	ND	---
26	Tetrachloroethene (PERC)	ND	ND	ND	ND	---
29	m+p-Xylene	0.02	ND	ND	0.00	-0.02
30	Styrene	0.00	0.00	0.00	0.01	0.01
32	o-Xylene	0.00	ND	ND	ND	-0.00
37	m-Dichlorobenzene	0.01	0.00	0.00	0.00	-0.01
38	p-Dichlorobenzene	0.01	0.00	0.00	0.00	-0.01
39	o-Dichlorobenzene	0.01	0.00	0.00	0.00	-0.01

(a) Δ(7-1) is the concentration change between day 1 and day 7.
(b) ND = Not Detected.

TABLE I-3.8.   TAC CONCENTRATIONS FOR ZERO AIR STORAGE STUDY – SIS CANISTERS

#	Compound	Fill ppb	Average Concentration (ppb)			
			Day 2	Day 4	Day 7	Δ(7-1)a
1	Dichlorodiflouromethane (Freon-12)	0.01	0.02	0.01	0.01	-0.00
4	Vinyl Chloride	0.00	NDb	0.01	ND	0.00
8	1,1-Dichloroethene	ND	ND	ND	ND	---
9	Dichloromethane (DCM)	ND	ND	ND	ND	---
11	1,1,2-Trichloro-1,2,2-Trifluoroethane	0.05	0.03	0.04	0.04	-0.01
14	Trichloromethane (CHCL3)	ND	ND	ND	ND	---
15	1,2-Dichloroethane (EDC)	ND	ND	ND	ND	---
16	1,1,1-Trichloroethane (TCEA)	0.03	0.05	0.04	0.03	-0.01
17	Benzene	0.02	0.03	0.04	0.05	0.03
18	Carbon Tetrachloride (CCL4)	ND	ND	ND	ND	---
20	Trichloroethene (TCE)	ND	ND	ND	0.00	0.00
24	Toluene	0.04	0.03	0.05	0.06	0.02
25	1,2-Dibromoethane (EDB)	ND	ND	ND	ND	---
26	Tetrachloroethene (PERC)	ND	ND	ND	ND	---
29	m+p-Xylene	0.02	ND	ND	ND	-0.02
30	Styrene	0.00	0.00	0.00	0.00	-0.00
32	o-Xylene	0.00	ND	ND	ND	-0.00
37	m-Dichlorobenzene	0.01	0.01	0.01	0.00	-0.01
38	p-Dichlorobenzene	0.01	0.01	0.01	0.00	-0.01
39	o-Dichlorobenzene	0.01	0.01	0.00	0.00	-0.01

(a)   Δ(7-1) is the concentration change between day 1 and day 7.
(b)   ND = Not Detected.

Clearly the largest and most significant increase was the level of Benzene (14-20 ppb).

One of the more unusual results is that the three dichlorobenzene compounds showed a significant decrease in concentrations when the stored sample contained TAC concentrations at the 0.5 ppb. level. On the other hand, the zero air samples were apparently contaminated by these chemicals. These results are consistent with the theory that the heavier compounds tend to adhere to the walls of the bags and may remain even after the bags are cleaned.

Plots of the measured concentrations versus storage day for each of the four bag samples and four canister samples are presented in Appendix I-B2. The letters A through H represent the measured concentrations in the eight bag and canister samples and the numbers 1, 2, and 3 represent the measured concentrations obtained during the fill operation on day 1. Notice that the chemicals in the canisters were not detected (0.000 ppb) except when we found trace levels during the fill operation. The only exception was for trichloromethane which was found in only one of the four canisters (CB2) at a level of 0.01 ppb on days 4 and 7. This may be due to contamination during the measurement process. In any case, this level is insignificant compared to the average ambient level of 0.13 ppb.

3.3 Bag/Can Summary

The bag/can zero air and 0.5 ppb level experiments showed the following. Statistical analysis of the data using linear regression analysis demonstrated that there was no significant change in any of the chemical concentrations for samples stored in canisters for seven days at either the 0.5 ppb or 0.0 ppb level. However regression analysis demonstrated that there were several statistically significant changes in chemical concentrations for samples stored in Tedlar bags. The largest and most significant increase was the level of benzene. During the earlier 0.5 ppb studies, the net increase in benzene over the seven day storage period was 75 to 85 ppb. During the subsequent zero level experiments, the net increase was 14 to 20 ppb. In general, the NLB and SLB bags showed significant changes in the same chemicals in both the 0.5 ppb and 0.0 ppb experiments.

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CHAPTER II. STATISTICAL ANALYSES OF ARB'S FIELD TEST DATA

1.0 Introduction

As part of our evaluation of ARB's sampling procedures and equipment, we identified two studies conducted by ARB that provided useful data for characterizing transportation and storage effects on TAC concentrations in actual field samples. In Section 2.0 we present our statistical analyses of the data from ARB's Bag Swap study which was conducted during 1987. The study was originally designed to identify differences between the analytical systems of the Northern (NLB) and Southern (SLB) laboratory branches. However, the data obtained from the study proved to be even more valuable for estimating the transportation and storage effects on TAC samples in Tedlar bags. The second study, discussed in Section 3.0, was the Bag/Can Collocated Sample study conducted by SLB in 1987. This study provided data comparing chemical analyses of collocated field samples collected in Tedlar bags and stainless steel canisters.

2.0 ARB Bag Swap Study

2.1 Background

ARB conducted the bag swap study in 1987 to determine whether or not there are changes in TAC concentrations in Tedlar bags due to transportation and storage effects and to estimate differences between NLB and SLB analytical measurements. This statistical analysis is an extension of the Perchloroethylene (PERC) Duplicate Analysis study performed by the ARB (Mike Poore memo: 1/11/88) in which the transportation effects on PERC levels were identified. Battelle obtained the full dataset from this study in order to evaluate transportation effects on nine TACs including PERC. The nine TACs studied are: dichloromethane (DCM), trichloromethane (CHCL3), 1,2-dichloroethane (EDC), 1,1,1-trichloroethane (TCEA), tetrachloromethane (CCL4), trichloroethene (TCE), 1,2-dibromoethane (EDB), PERC, and benzene.

2.2 Study Design and Database

The Bag Swap data used in this study come from an ARB database that contains triplicate analyses of field samples collected during the period from December 1986 to November 1987. The four steps that the ARB laboratories followed in conducting the study were

(1) Randomly select an ambient sample,

(2) Measure the TAC concentration level (initial analysis),

(3) Send the bag to the other laboratory for a second analysis, and

(4) Perform a third analysis of the sample after the bag is returned.

The concentration levels were measured in parts per billion (ppb), and the same transportation system was used to ship the bags between the laboratories. The median time between the initial and final sample analyses for each laboratory was 8 days.

In our statistical analysis we selected only data for which all three chemical analyses exist for each TAC. If one or more analysis results were missing, all the data for the specific TAC were deleted. There were 15 NLB samples and 31 SLB samples used in this study. The NLB and SLB data were analyzed separately. The data used for this analysis are presented in Appendix II-A.

2.3 Statistical Analysis

In this analysis we statistically analyzed the differences between TAC concentration levels from the initial and final analyses to determine if there are transportation effects. We also compared measurements between the NLB and SLB laboratories.

2.3.1 Transportation and Storage Effects. The objective of this analysis was to determine if there are significant changes in TAC concentrations in Tedlar bags due to transportation and storage effects. We made within-laboratory comparisons by estimating the median difference between the initial and final analyses and the percent of samples where

there was an increase in TAC concentration between analyses. The results of the within-laboratory comparisons for the NLB and SLB laboratories are summarized in Tables II-2.1 and II-2.2. These tables list for each of the nine TACs:

- The average initial concentration

- The median change in concentration between the initial and final analyses

- The three largest absolute changes in concentration between the initial and final analyses

- The total number of samples (with non-missing data) analyzed

- The percent of samples where an increase in concentration between the initial and final analyses is detected (samples where no change was measured were not included in this calculation)

- A flag to indicate whether or not the median increase is statistically different from zero (or the percent of increases is different from 50) at the .05 level of significance.

A number of the differences that we analyzed were outside the normal range of the data. Because of these outliers, a nonparametric sign test was used to test whether or not the median change in concentration was statistically different from zero. A t-test was also used to test whether or not the mean differences were statistically significant. However, we reported our results based on the sign test because the t-test was often inappropriate due to the large number of statistical outliers.

We found significant increases in concentration levels of DCM, TCEA, TCE, and PERC due to transportation of the Tedlar bags originating from NLB laboratories. We also found significant increases in concentration level of DCM, TCEA, TCE, PERC, $CHCL_3$, and CCL_4 due to transportation of the Tedlar bags originating from SLB laboratories and a significant decrease in concentration of EDC.

Another factor we looked at in this study was whether or not the date or season of the transportation of the samples affected the concentration levels in the Tedlar bags. One might expect, for example, higher differences in the summer months due to a higher temperature during transportation. However, we did not find significant trends in the data.

TABLE II-2.1. SUMMARY OF THE BAG SWAP ANALYSIS RESULTS - NLB BAG SAMPLES

Compound		Avg. Init. Concentration (ppb)	Median Change (ppb)	Highest Change[1] (ppb)			Number of Samples	Percent of Increases
#	Name			1st	2nd	3rd		
9	Dichloromethane (DCM)	1.12	0.40*	1.50	1.20	1.20	14	85*
14	Trichloromethane (CHCL3)	0.38	0.00	0.50	-0.03	0.00	6	50
15	1,2 - Dichloroethane (EDC)	0.10	0.00	ND	ND	ND	11	--
16	1,1,1-Trichloroethane (TCEA)	0.63	0.09*	2.70	0.42	0.40	12	91*
18	Tetrachloromethane (CCL4)	0.09	0.00	0.04	0.01	0.01	13	38
20	Trichloroethene (TCE)	0.17	0.03*	1.44	0.13	0.11	14	92*
25	1,2-Dibromoethane (EDB)	0.01	0.00	ND	ND	ND	14	--
26	Tetrachloroethene (PERC)	0.17	0.03*	0.35	0.10	0.10	14	100*
17	Benzene	2.79	0.00	-1.15	0.70	0.50	13	50

ND   Not Detected.
*   Indicates that the median increase is different from zero at .05 level of significance.
(1) Highest absolute changes are reported.

TABLE II-2.2. SUMMARY OF THE BAG SWAP ANALYSIS RESULTS - SLB BAG SAMPLES

#	Compound Name	Avg. Init. Concentration (ppb)	Median Change (ppb)	Highest Change[1] (ppb)			Number of Samples	Percent of Increases
				1st	2nd	3rd		
9	Dichloromethane (DCM)	1.65	0.90*	11.50	10.08	6.40	29	86*
14	Trichloromethane (CHCL3)	0.12	0.02*	0.86	0.21	0.20	31	73*
15	1,2 - Dichloroethane (EDC)	0.46	-0.05*	-1.30	1.08	-1.00	29	20*
16	1,1,1-Trichloroethane (TCEA)	2.82	1.45*	20.20	16.80	9.62	30	87*
18	Tetrachloromethane (CCL4)	0.10	0.01*	3.13	0.16	0.12	31	71*
20	Trichloroethene (TCE)	0.21	0.05*	19.70	1.17	0.86	30	83*
25	1,2-Dibromoethane (EDB)	0.01	0.00	-0.03	-0.02	0.02	30	38
26	Tetrachloroethene (PERC)	0.62	0.24*	12.56	12.20	-2.30	30	89*
17	Benzene	3.29	0.20	2.40	2.30	1.90	27	54

* Indicates that the median increase is different from zero at .05 level of significance.
(1) Highest absolute changes are reported.

2.3.2. Between-Laboratory Comparisons. The objective of this analysis was to determine if there are significant differences between the measured concentrations from the northern and southern laboratories. Although the comparison of laboratory analysis results was not a primary objective of our program it is important to be aware that these differences may exist when studying storage effects.

Our statistical analysis was based on the changes in estimated concentration levels between the initial and second analyses performed on each sample. Table II-2.3 shows the percent of samples in which there was an increase in concentration between analyses. For example, we found SLB had higher measured concentration of DCM than NLB in 85.7 percent (12 of 14) of the samples originating from NLB. Statistically, this percentage was significantly higher than the 50 percent level which one would expect if there were no differences between laboratories.

These results, along with the within-laboratory results, show that the analyses from the SLB laboratory are generally higher than those from the NLB laboratory. The only notable exception is benzene.

The existence of a laboratory bias is especially evident when these results are combined with those from the previous section in which we demonstrated that a transportation effect exists for certain TACs. From Table II-2.3 we see that there is a significant decrease in measured concentrations of several chemicals in SLB samples between the initial (SLB) and second (NLB) measurements. In the previous section we found that there was a significant increase between the initial and final (both SLB) measurements for most of these same compounds. Because it is doubtful that the concentration levels decreased during transportation from the SLB laboratory to the NLB laboratory and then significantly increased during transportation back to the SLB laboratory, a difference in the NLB and SLB measurement systems probably exists. Also, the percent of TAC concentration increases in samples from the NLB laboratories analyzed by SLB laboratories is generally higher than the within laboratory percent of increases estimated earlier for the NLB laboratory.

TABLE II-2.3. PERCENT OF INCREASES IN CONCENTRATION LEVEL BETWEEN LABORATORIES

Compound	NLB Samples		SLB Samples	
	No. of Samples	Percent Increase (SLB)	No. of Samples	Percent Increase (NLB)
DCM	14	85.7*	28	46.4
CHCL3	6	83.3*	31	0.0*
EDC	5	100.0*	19	0.0*
TCEA	11	81.8*	29	51.7
CCL4	13	46.2	30	46.7
TCE	14	85.7*	30	26.7*
EDB	1	100.0*	6	16.7
PERC	14	100.0*	28	14.3*
Benzene	11	18.2*	26	84.6*

* Indicates that the median increase is different from zero
  at 0.05 level of significance.

APPENDIX I-A


PLOTS OF MEASURED CONCENTRATION VERSUS TIME FOR
BAG/CAN STORAGE STUDY WITH 0.5 PPB TAC CONCENTRATIONS

PLOTS OF MEASURED CONCENTRATION VERSUS TIME FOR
BAG/CAN STORAGE STUDY WITH 0.5 PPB TAC CONCENTRATIONS

Plots are presented for each of the ARB selected chemicals showing the measured concentration in NLB and SLB bag samples during the seven day storage study. Quantitation was based on response factors calculated be averaging GC peak areas from the analyses of 4 canister samples. A common scale of 0 to 1.0 ppb is used for each chemical, except those whose measured concentrations exceeded 1.0 ppb.

#=1   Compound Name=dichlorodiflouromethane   Torget Concentration (ppb)=0.49

Concentration-ppb

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

0   1   2   3   4   5   6   7   8

Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

IA-2
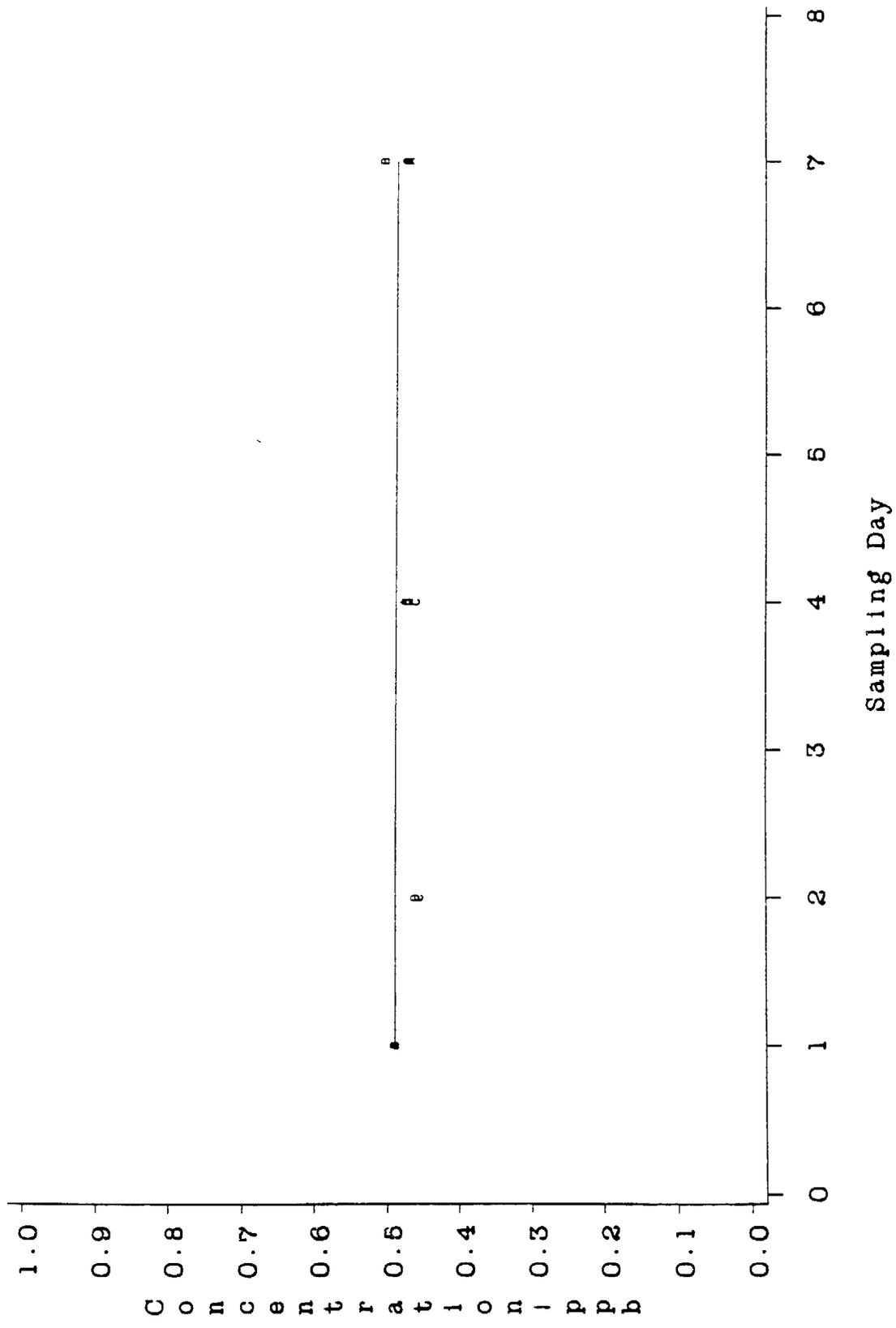
#=4   Compound Name=vinyl chloride   Target Concentration (ppb)=0.88

Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

IA-3
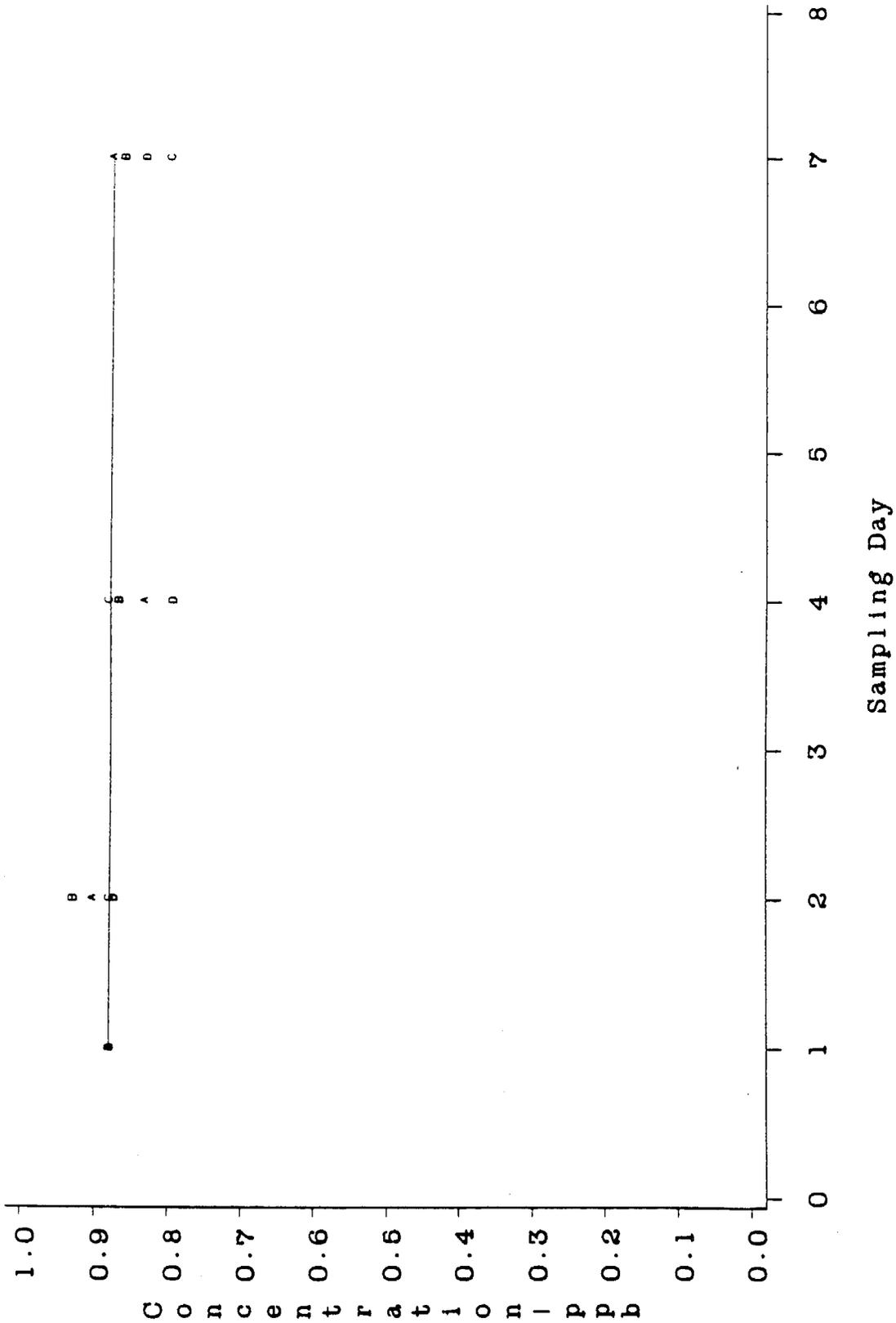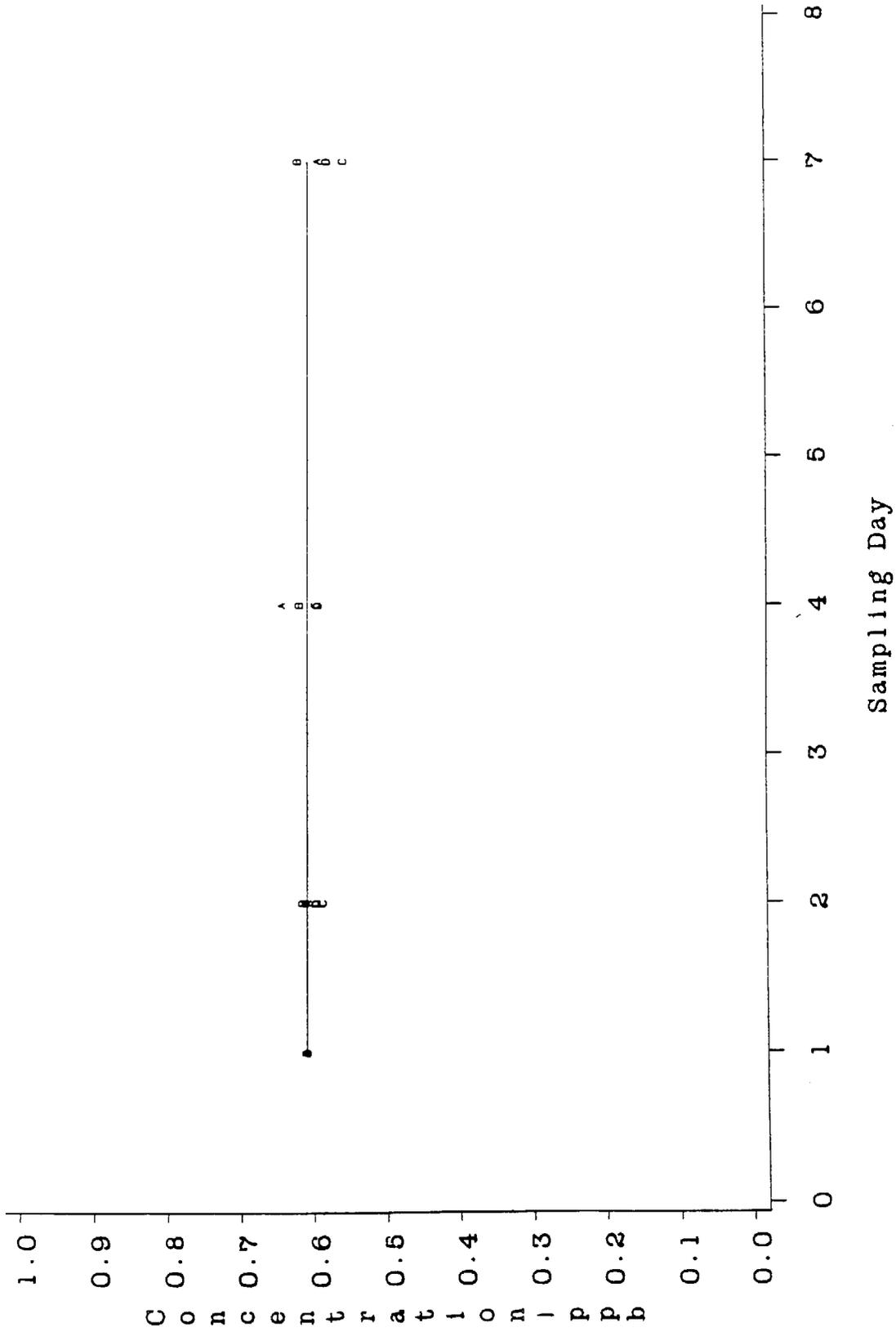
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

#=9   Compound Name=dichloromethane   Target Concentration (ppb)=0.78
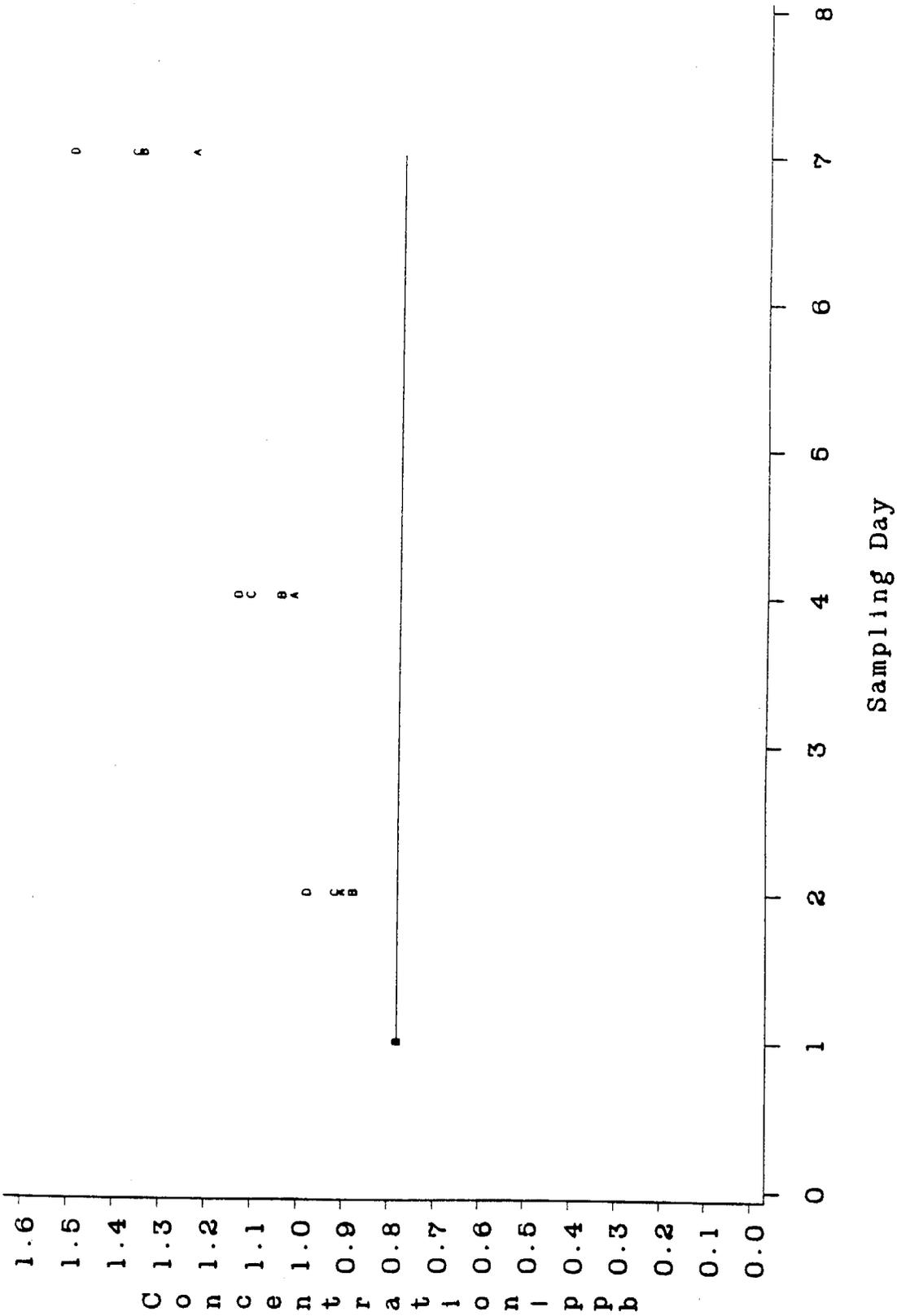
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

#=11   Compound Name=1,1,2-trichloro-1,2,2-trifluoroethane   Target Concentration (ppb)=0.52
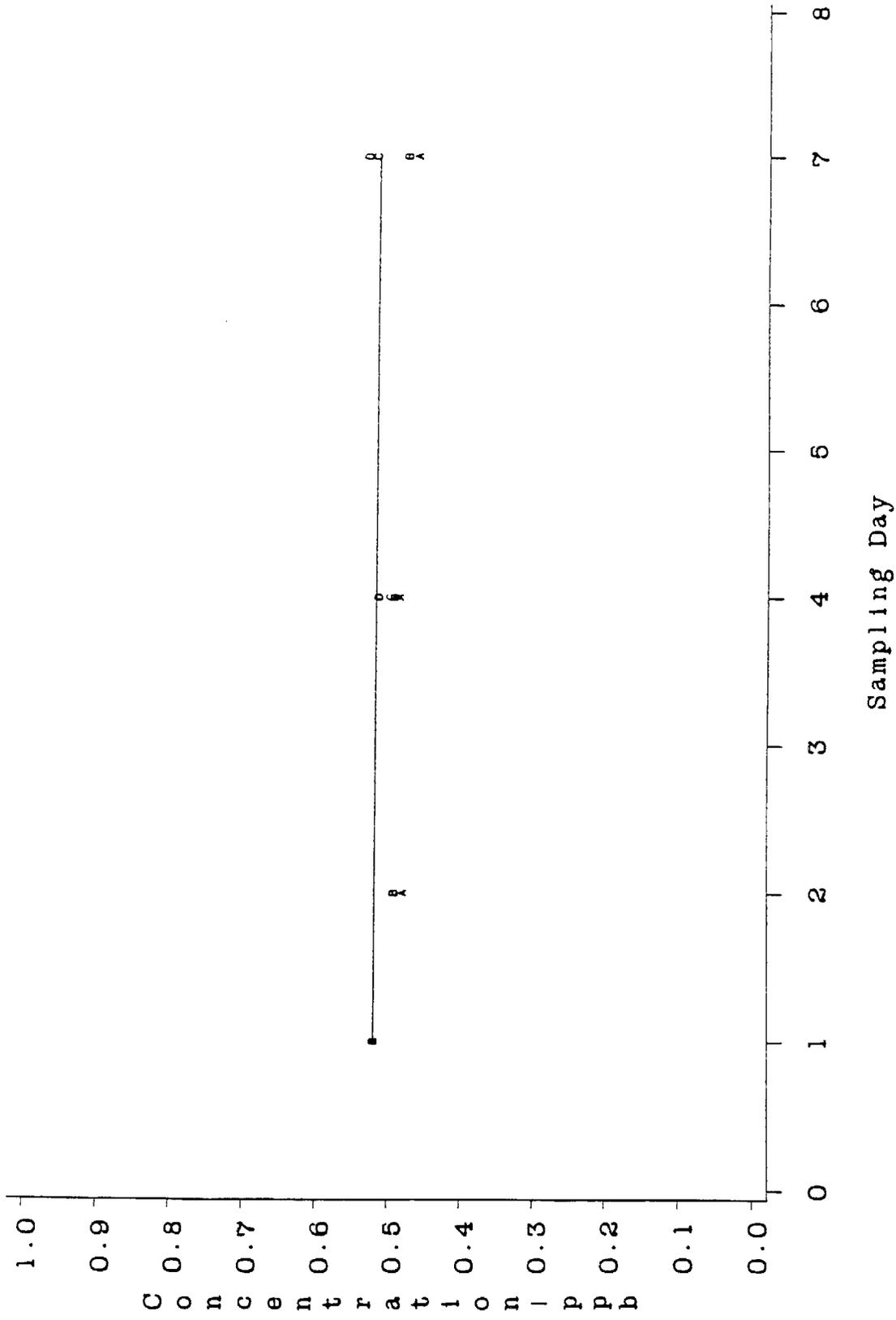
Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

IA-6

#=14   Compound Name=trichloromethane   Target Concentration (ppb)=0.66

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

Concentration-ppb

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0

0   1   2   3   4   5   6   7   8

Sampling Day
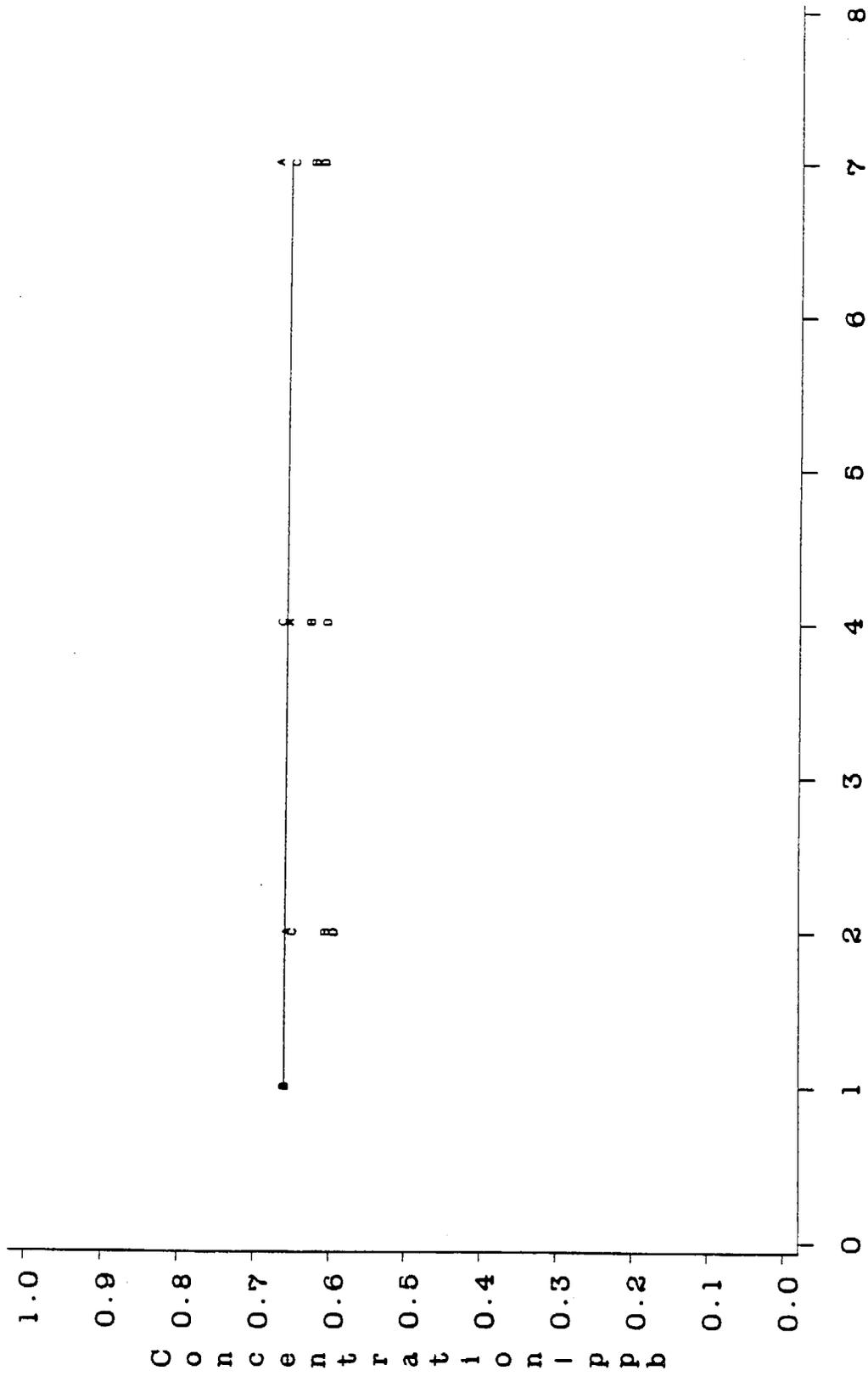
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2
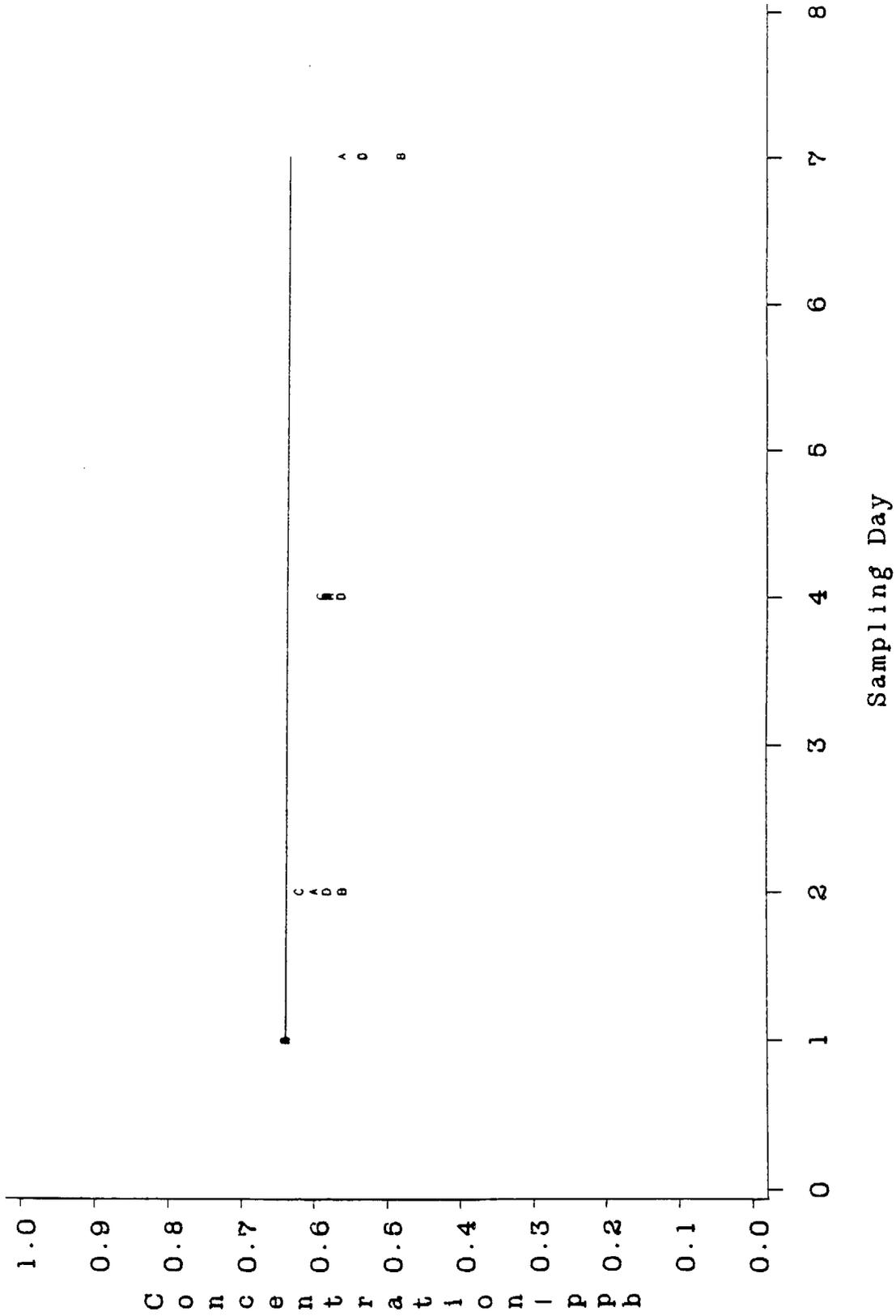
#=16   Compound Name=1,1,1-trichloroethane   Target Concentration (ppb)=0.51

Concentration - ppb

Sampling Day
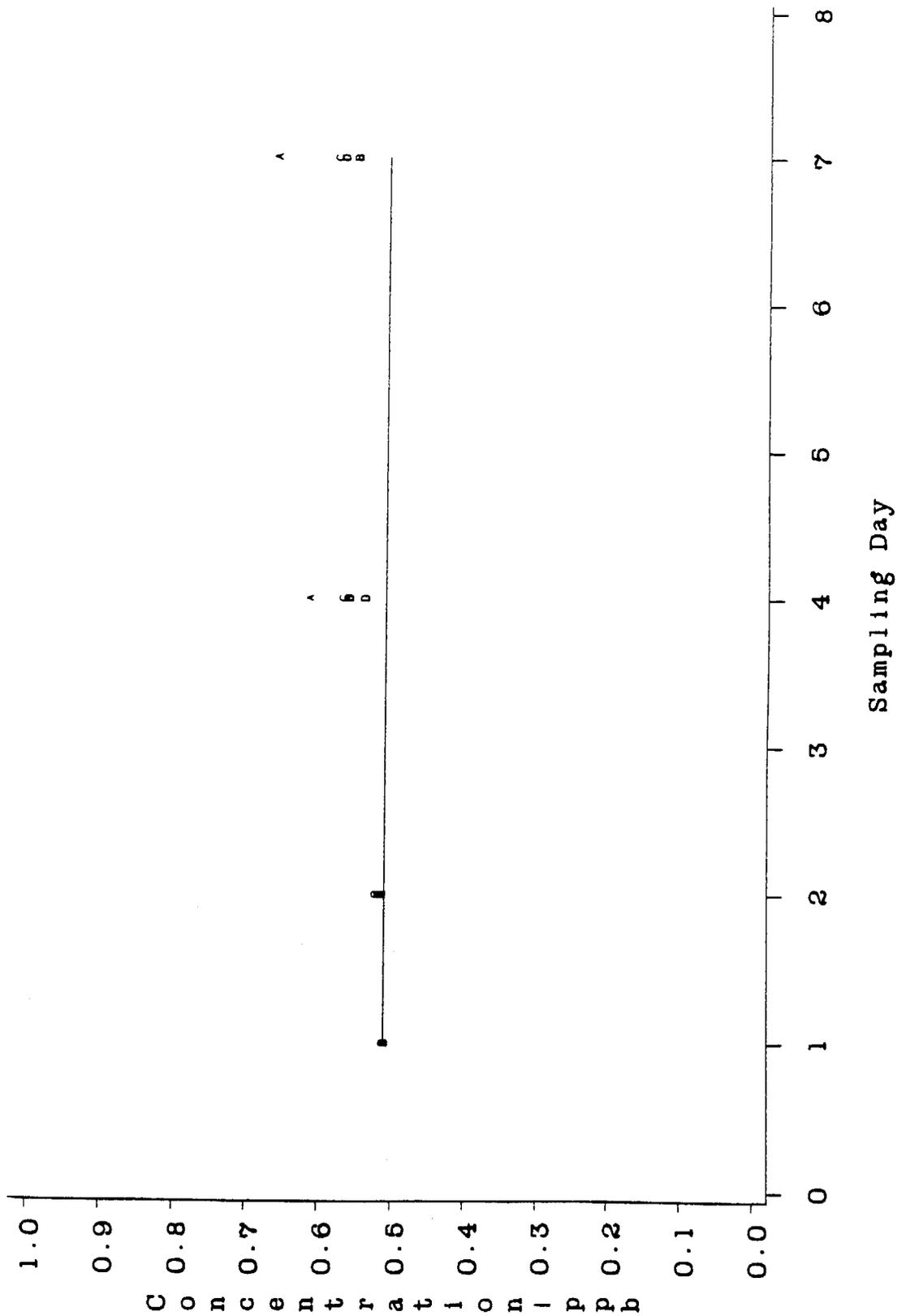
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

#=17   Compound Name=benzene   Target Concentration (ppb)=0.54


Sample Type   A=BN1   B=BN2   C=BS1   D=BS2
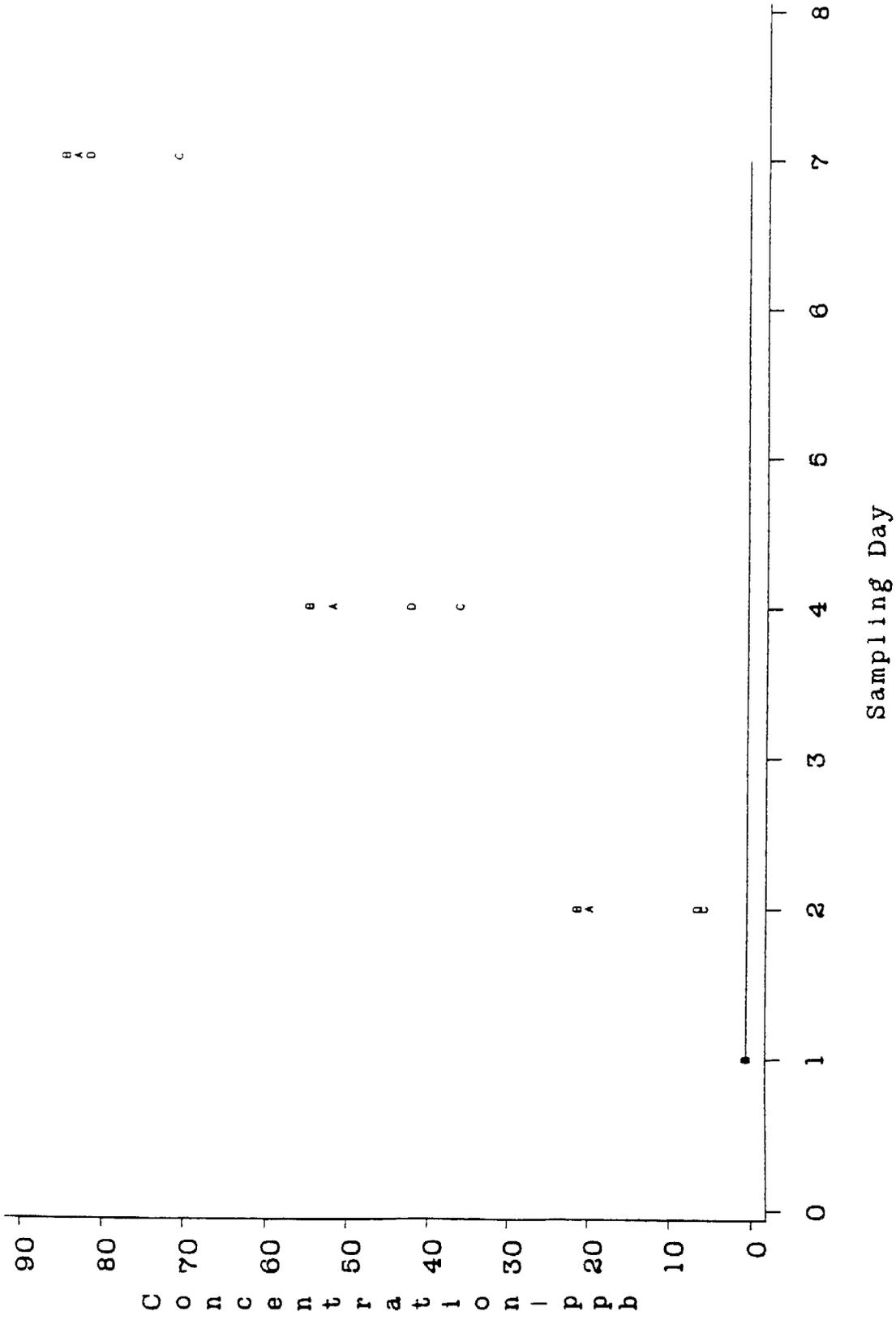
#=18   Compound Name=carbon tetrachloride   Target Concentration (ppb)=0.56
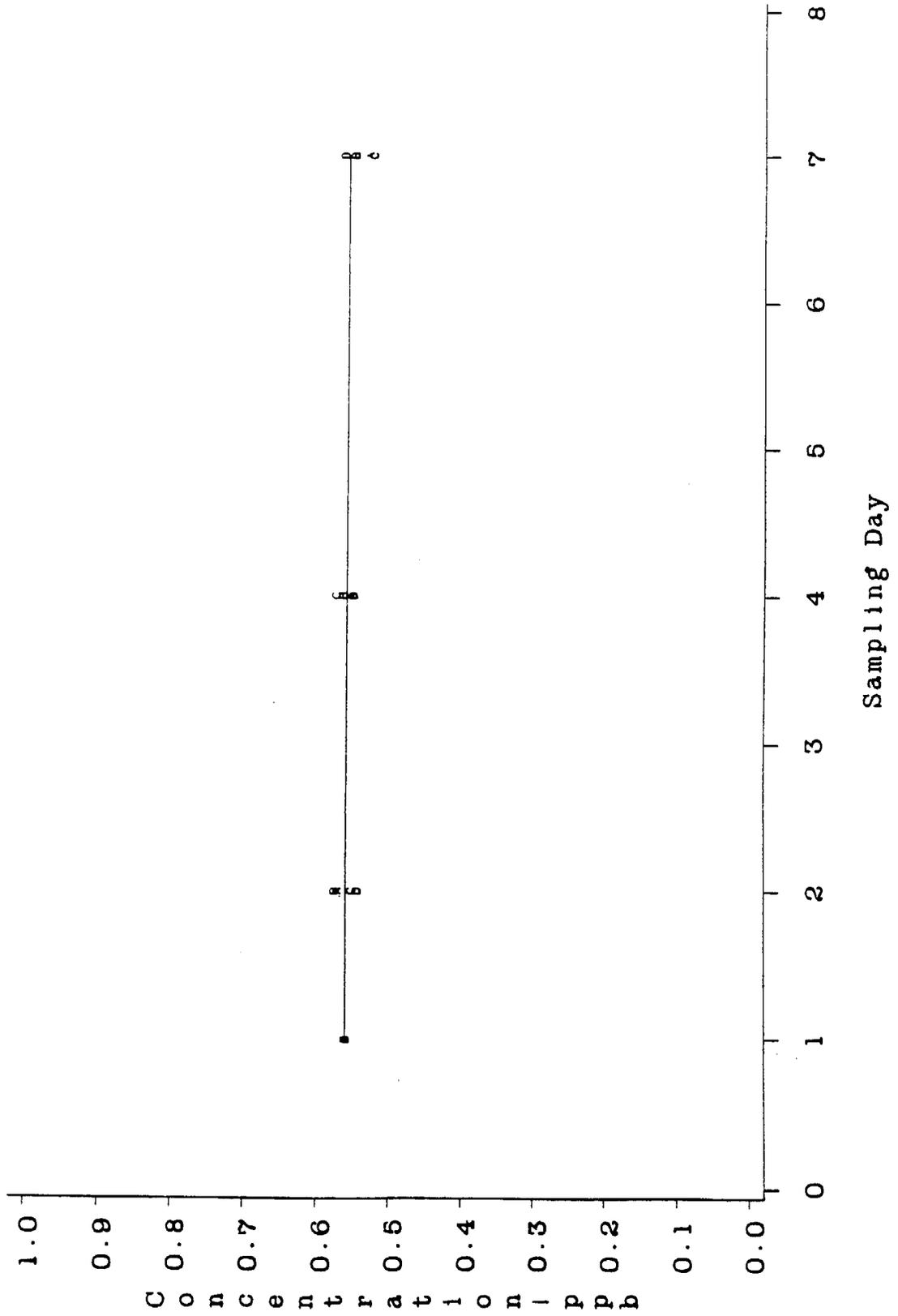
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

IA-11

#=20   Compound Name=trichloroethene   Target Concentration (ppb)=0.56

1.0 —

0.9 —

C 0.8 —
o
n 0.7 —
c
e
n 0.6 —
t
r 0.5 —
a
t
i 0.4 —
o
n 0.3 —
-
p 0.2 —
p
b 0.1 —

0.0 —

       0   1   2   3   4   5   6   7   8

                          Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

IA-12

#=24   Compound Name=toluene   Target Concentration (ppb)=0.47
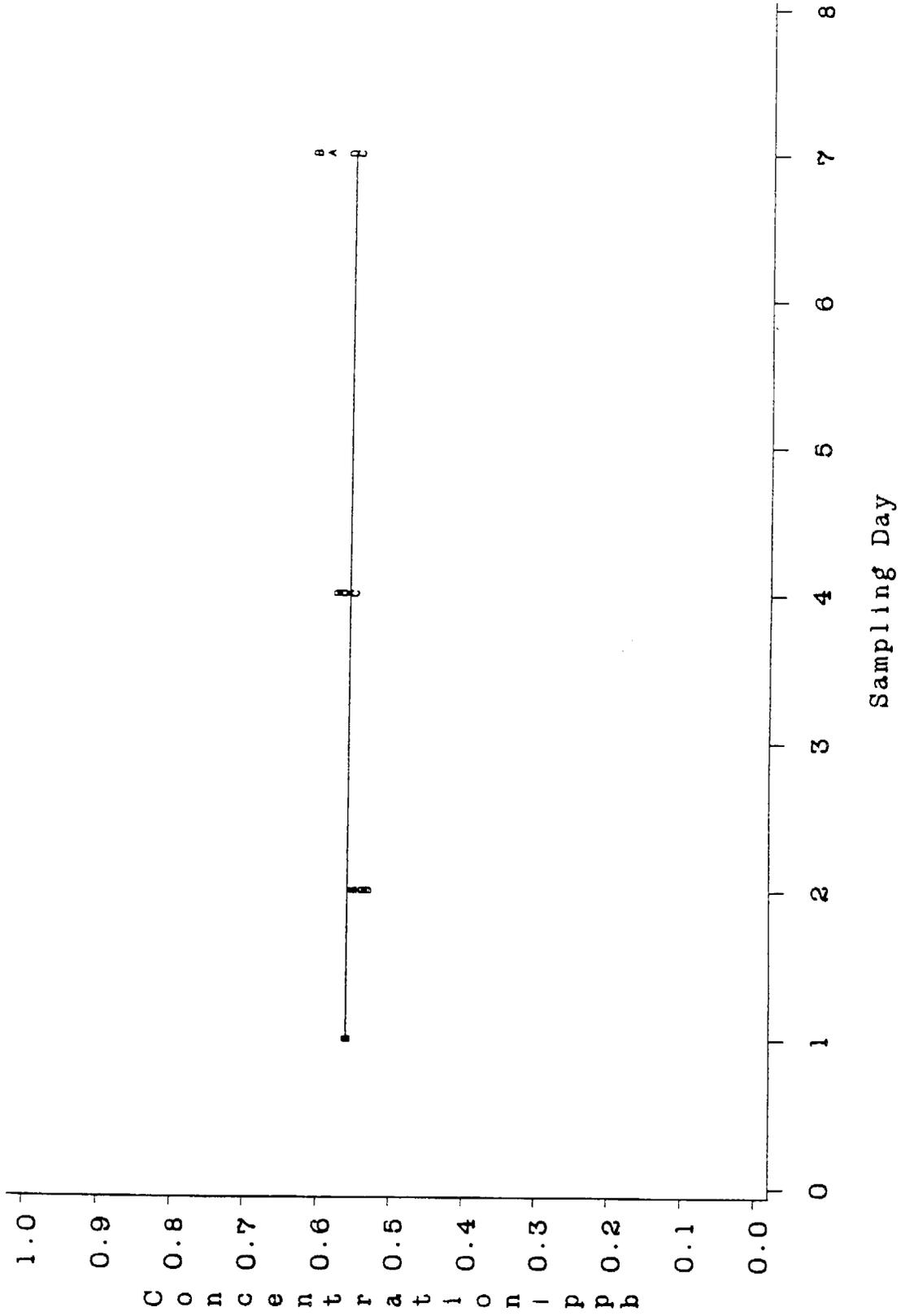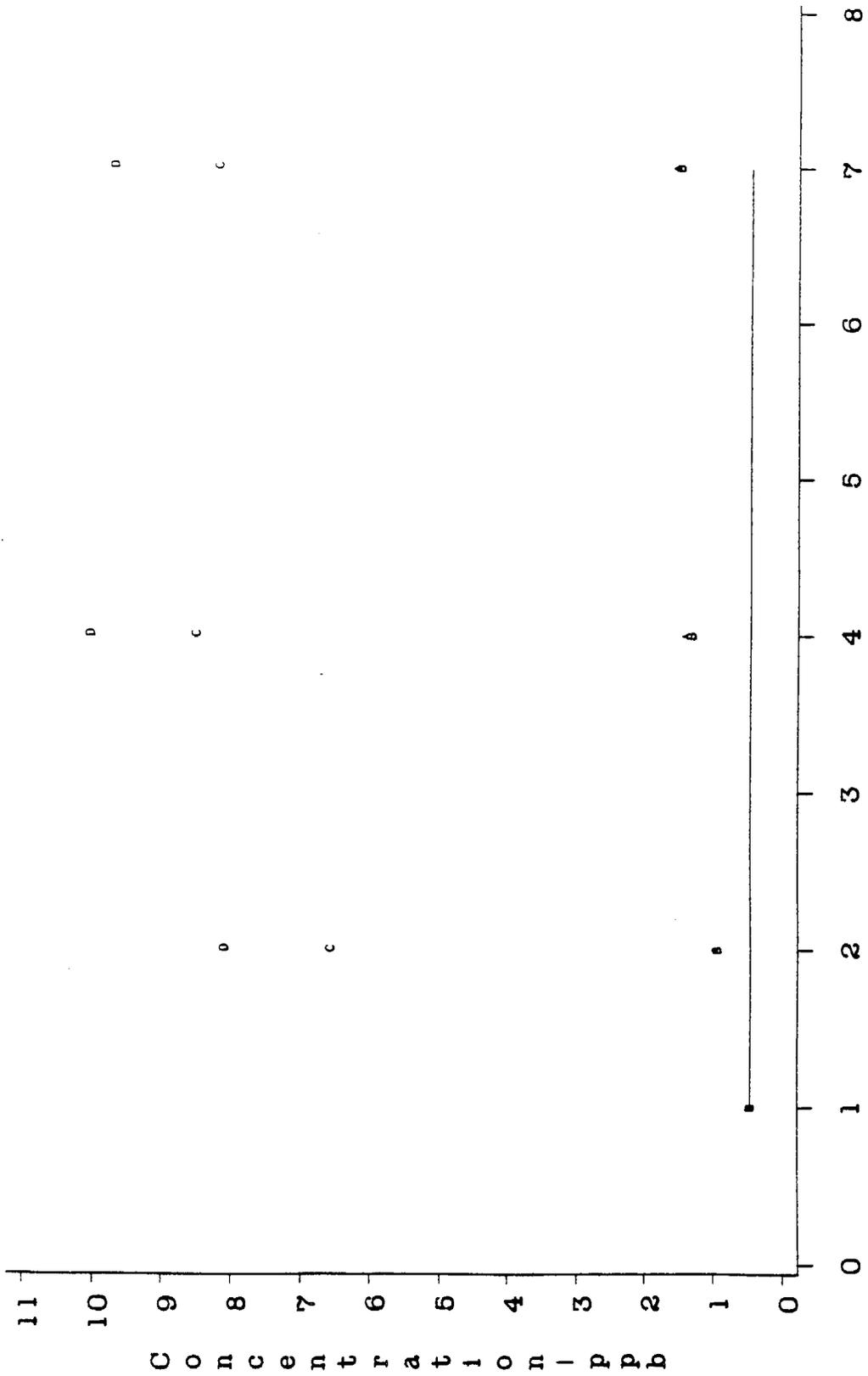
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

# = 25   Compound Name=1,2-dibromoethane   Target Concentration (ppb)=0.58

Concentration-ppb

Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

IA-14

#=26   Compound Name=tetrachloroethene   Target Concentration (ppb)=0.66

Concentration-ppb

Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

IA-15
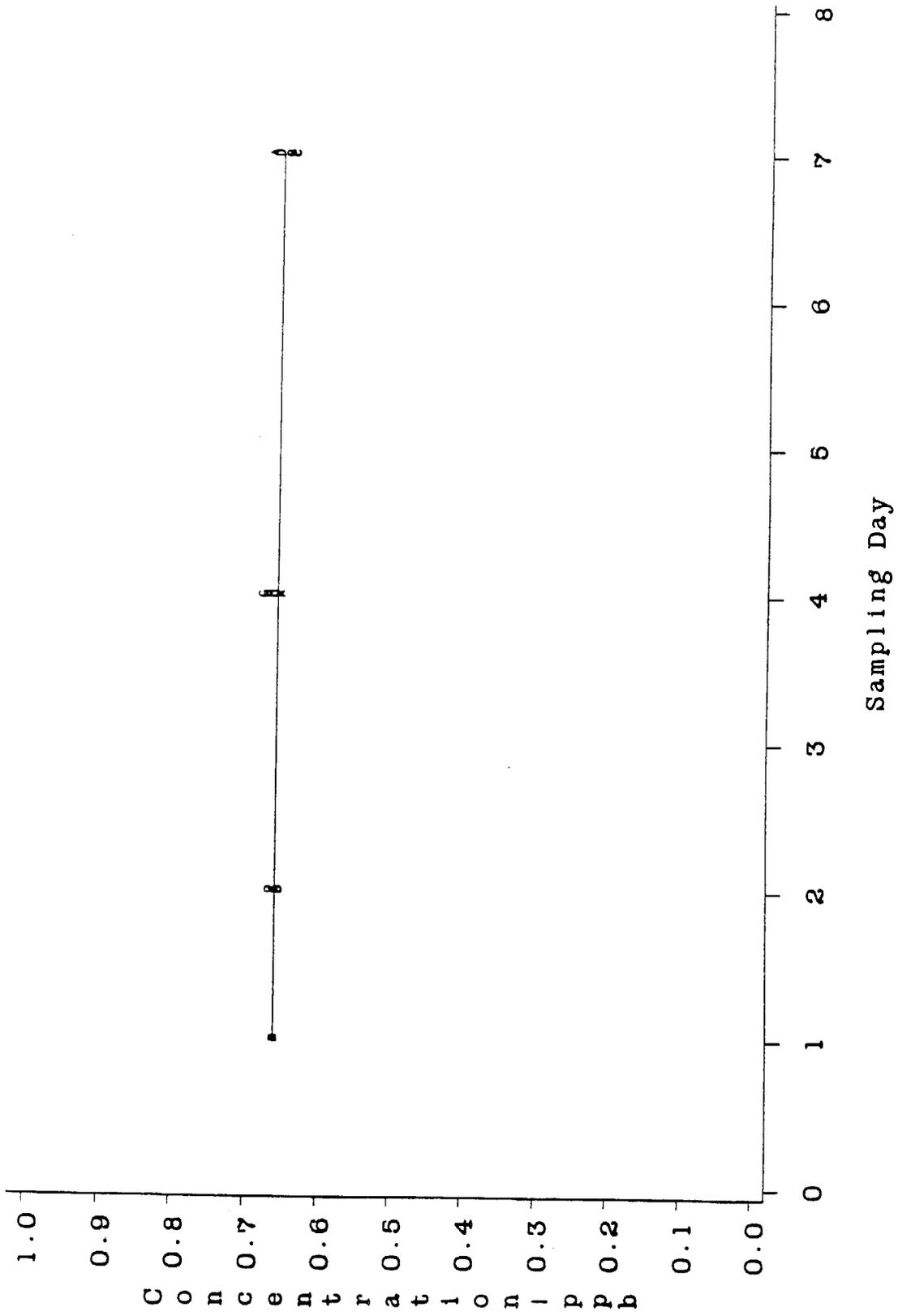
#=29   Compound Name=m+p-xylene   Target Concentration (ppb)=0.41

C 1.0
o 0.9
n
c 0.8
e
n 0.7
t
r
a 0.6
t
i 0.5
o
n 0.4
- 0.3
p
p 0.2
b 0.1
0.0

1.2
1.1

0   1   2   3   4   5   6   7   8

Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

IA-16
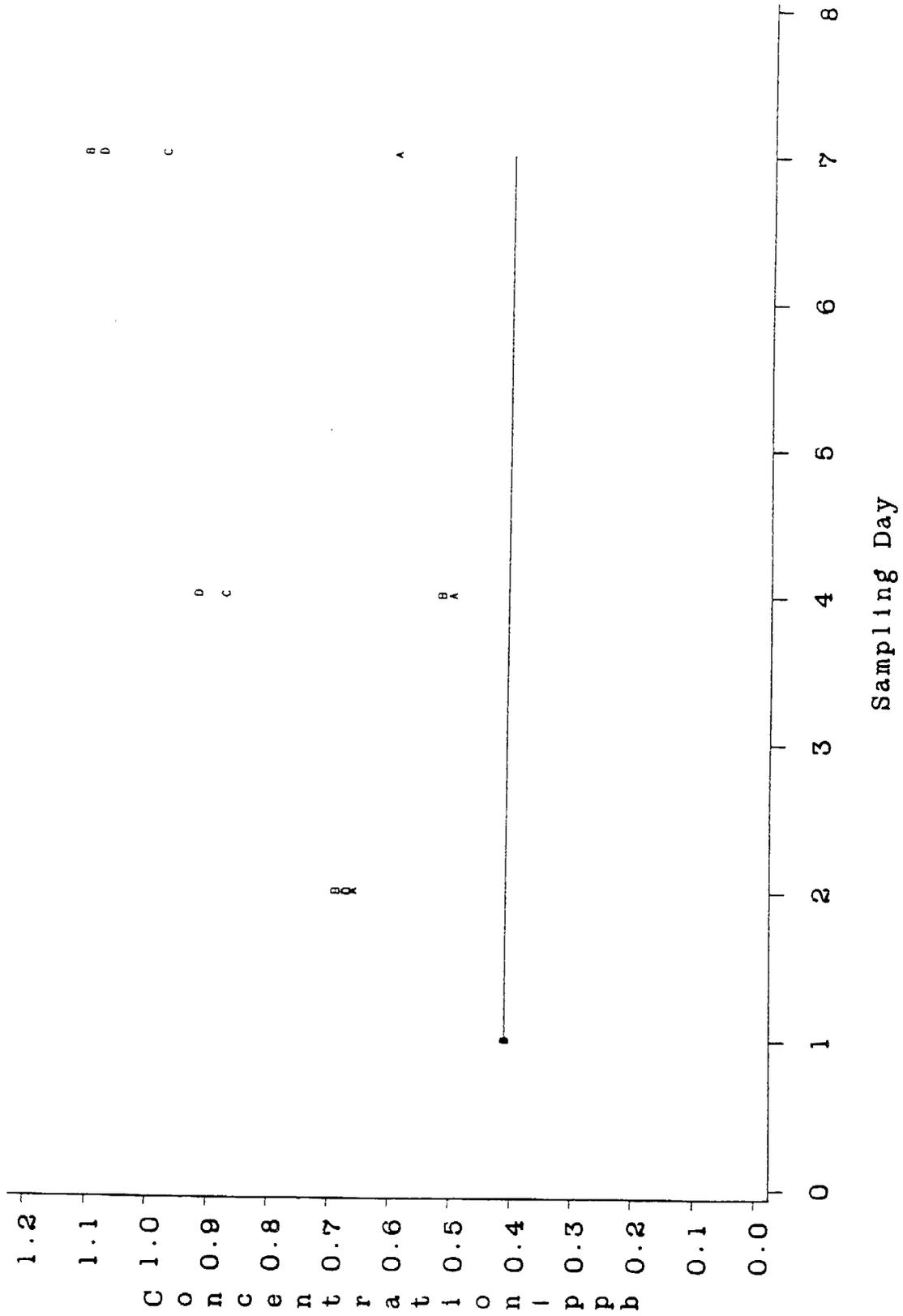
30   Compound Name--Styrene   Target Concentration (ppb) 0.45

Concentration (ppb)

```
0.93
0.88
0.83
0.78
0.73
0.68
0.63
0.58
0.53
0.48
0.43
```

```
0   1   2   3   4   5   6   7   8
```

Sampling Day
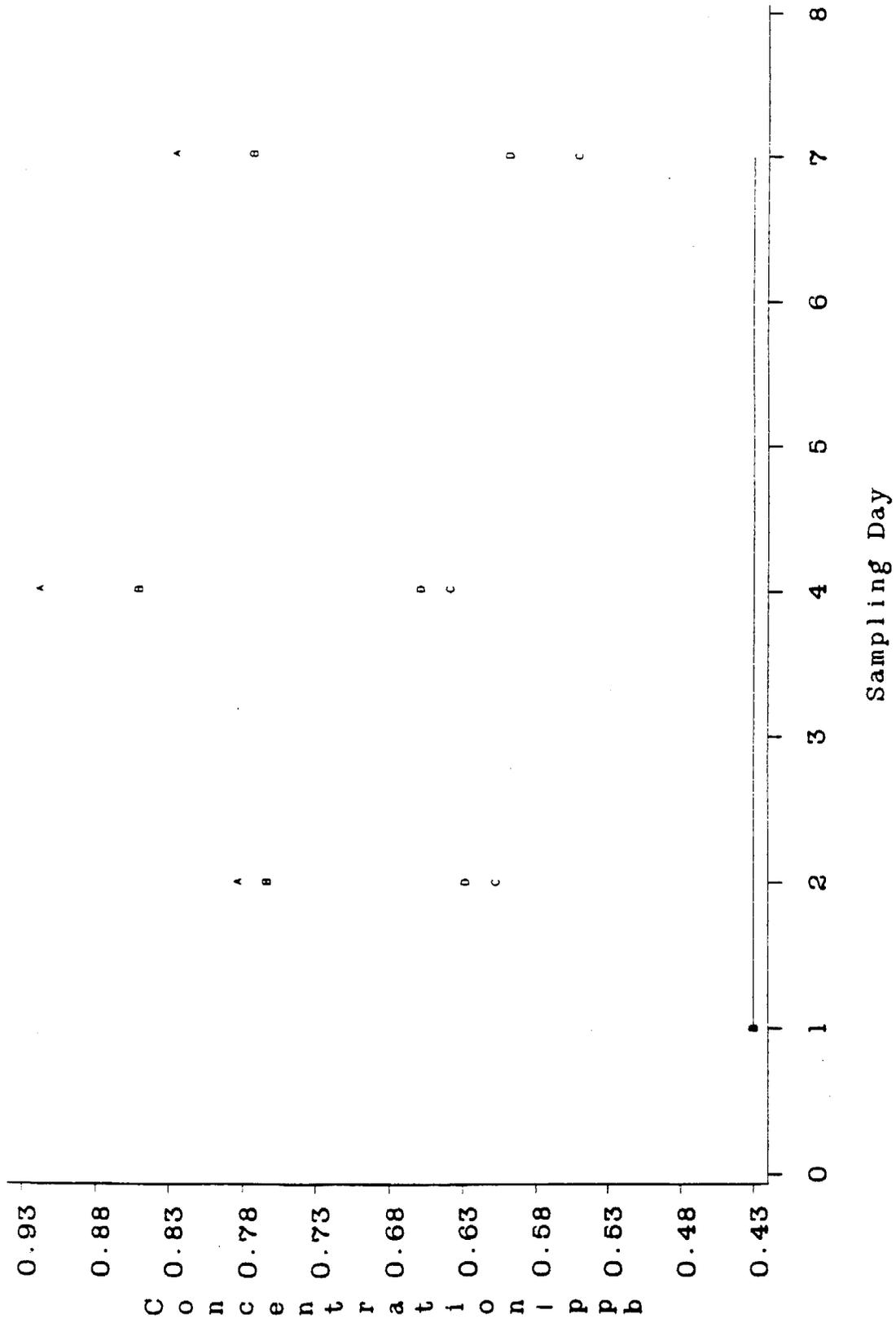
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2
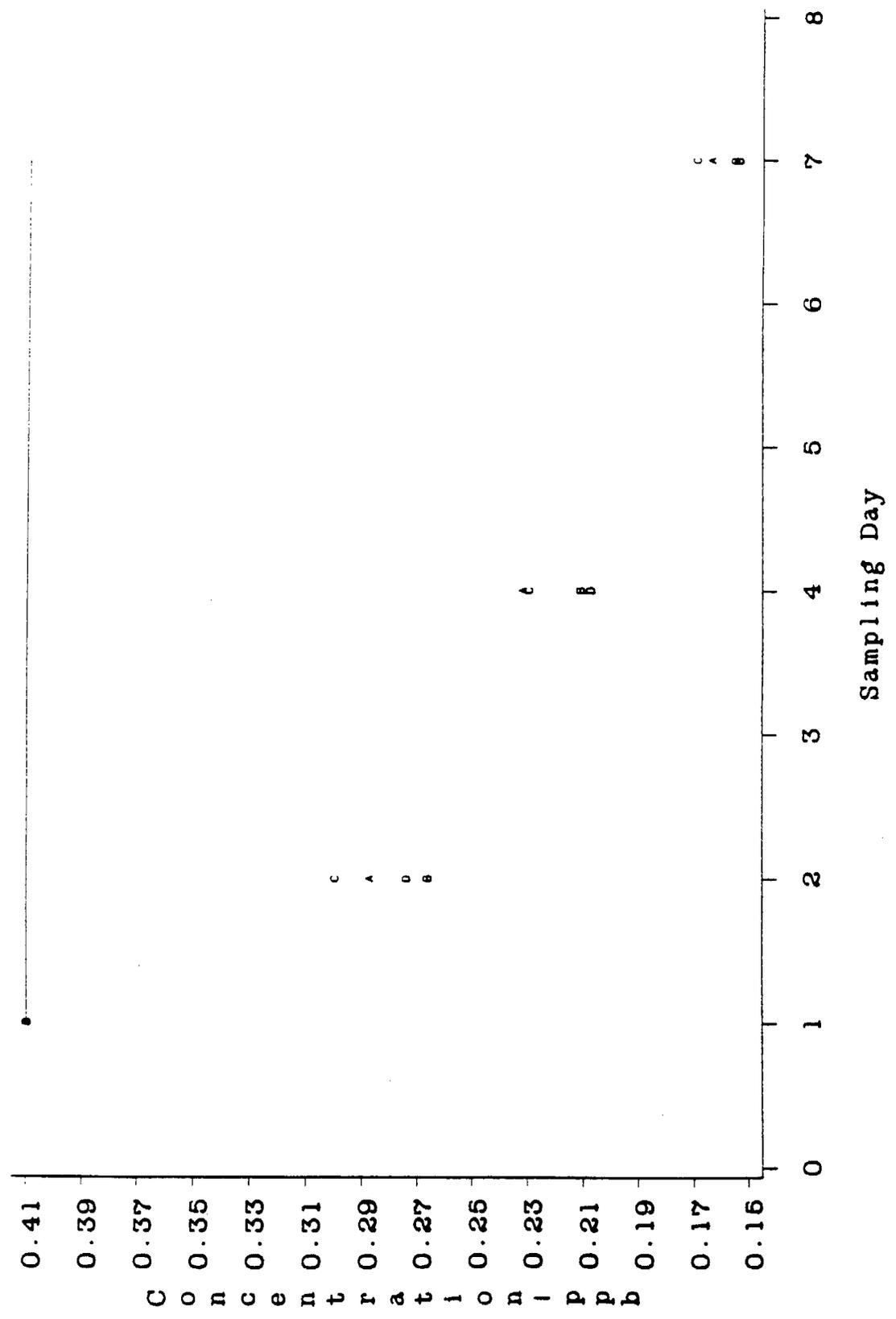
\# = 32   Compound Name=o-xylene   Target Concentration (ppb)=0 4 l.
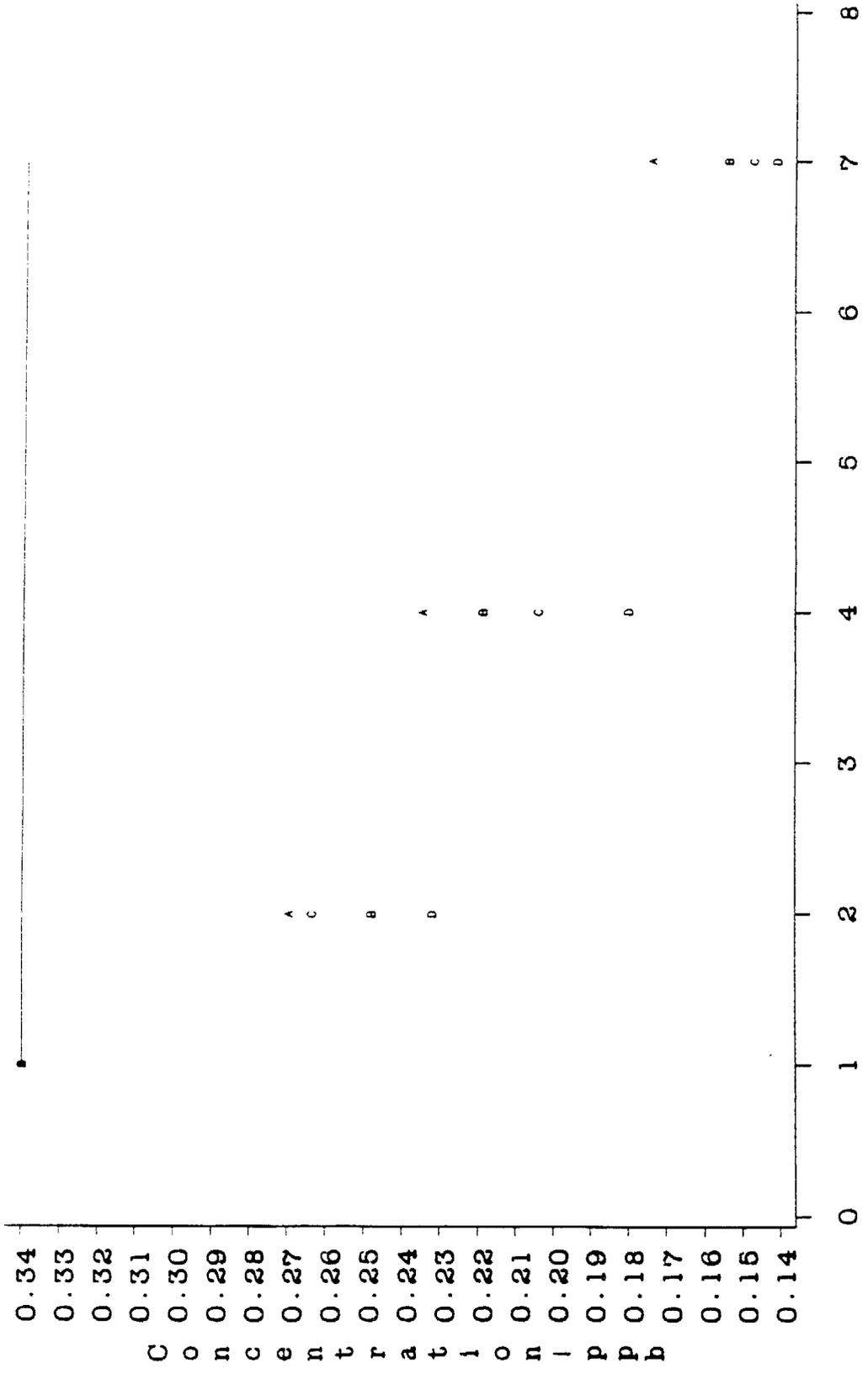
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

IA-18

#=37   Compound Name-m-dichlorobenzene   Target Concentration (ppb)=0.41

Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

N=38   Compound Name=p-dichlorobenzene   Target Concentration (ppb)=0.34

Concentration (ppb)

0.34
0.33
0.32
0.31
0.30
0.29
0.28
0.27
0.26
0.25
0.24
0.23
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0.14

Sampling Day

0   1   2   3   4   5   6   7   8

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

IA-20

#=39   Compound Name=o-dichlorobenzene   Target Concentration (ppb)=0.41
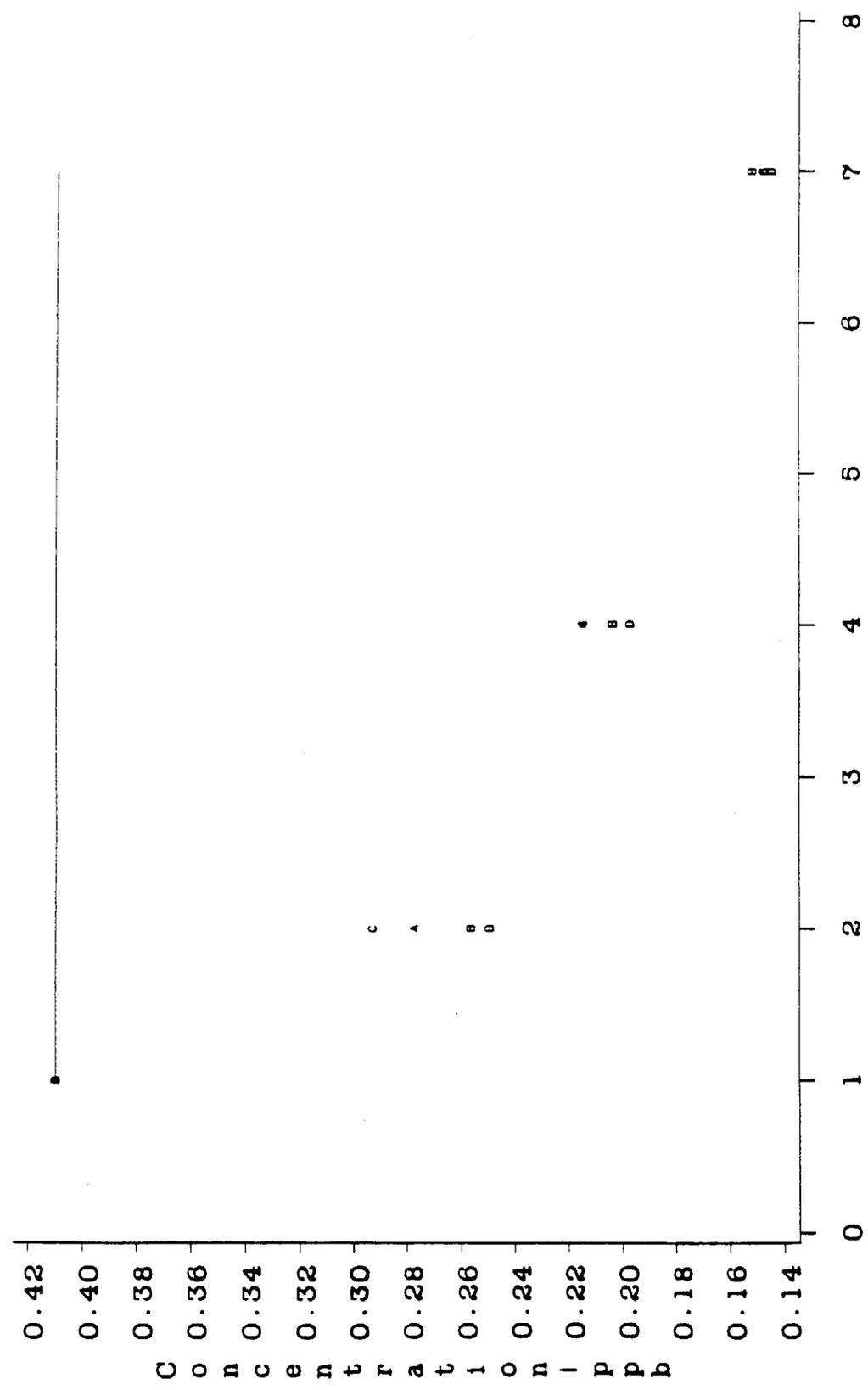
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2

APPENDIX I-B

PLOTS OF MEASURED CONCENTRATIONS VERSUS TIME
FOR BAG/CAN STORAGE STUDY WITH ZERO AIR

APPENDIX I-B

PLOTS OF MEASURED CONCENTRATIONS VERSUS TIME
FOR BAG/CAN STORAGE STUDY WITH ZERO AIR

      Plots are presented for each of the ARB selected chemicals showing
the measured concentrations in Tedlar bags and canisters during the seven
day storage study. Also shown are the background levels obtained from the
three QC samples on day one.

#=1   Compound Name=dichlorodiflouromethane

Concentration (ppb)

Sampling Day

Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
             1=QC1   2=QC2   3=QC3

IB-2
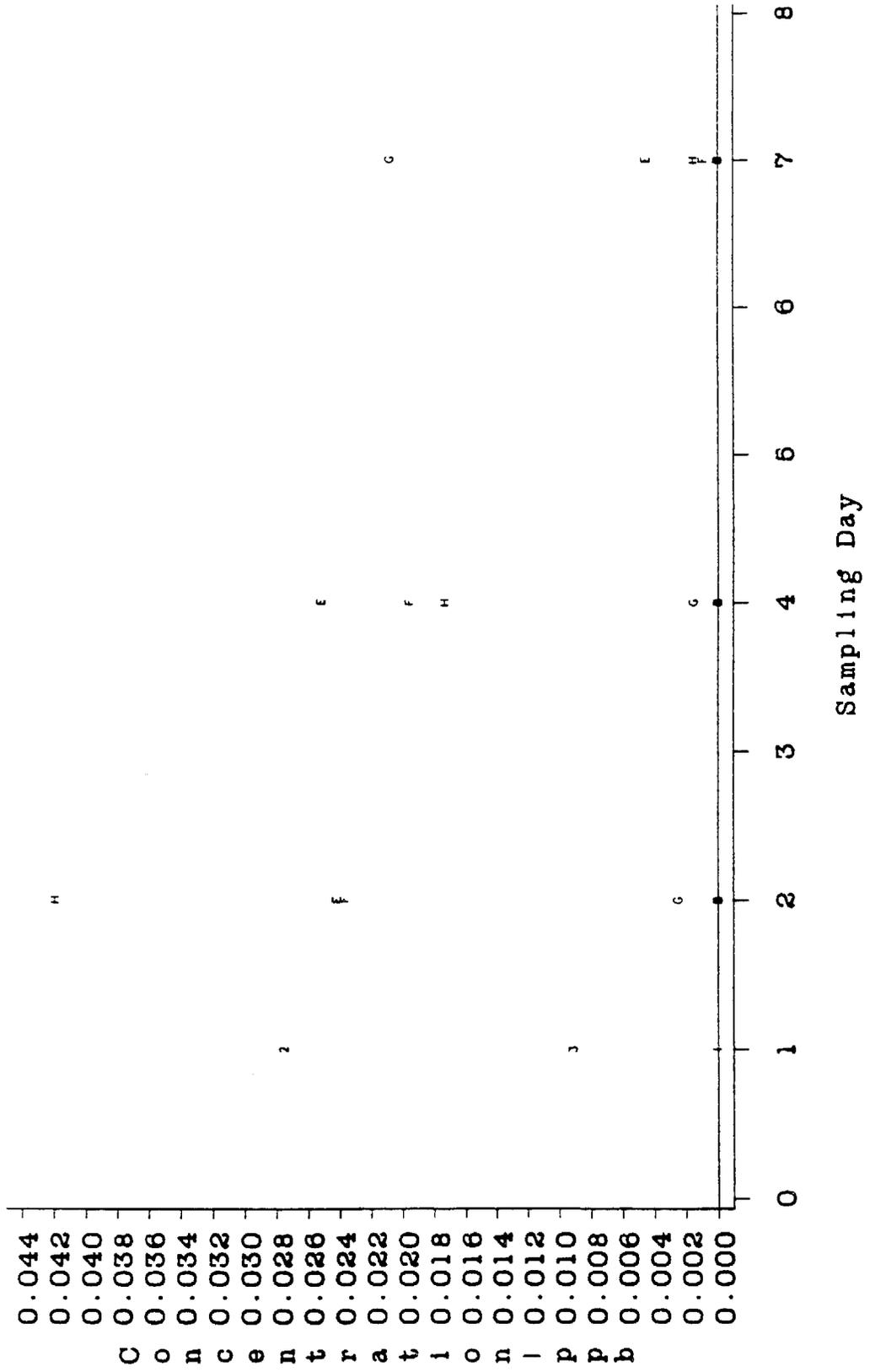
#=4   Compound Name=vinyl chloride

Sampling Day
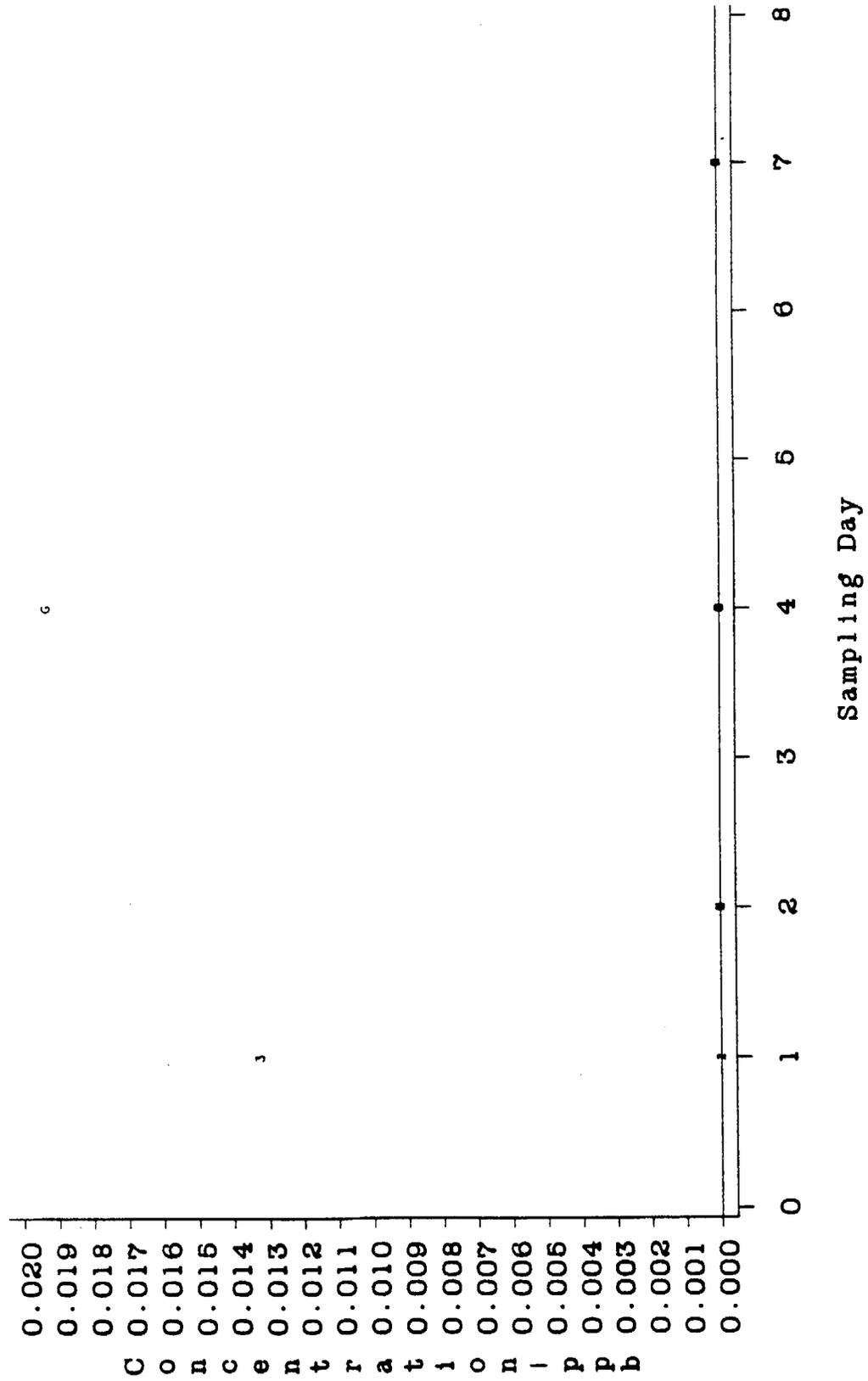
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2
              E=CB1   F=CB2   G=CS1   H=CS2
              1=QC1   2=QC2   3=QC3

#=8   Compound Name=1,1-dichloroethene
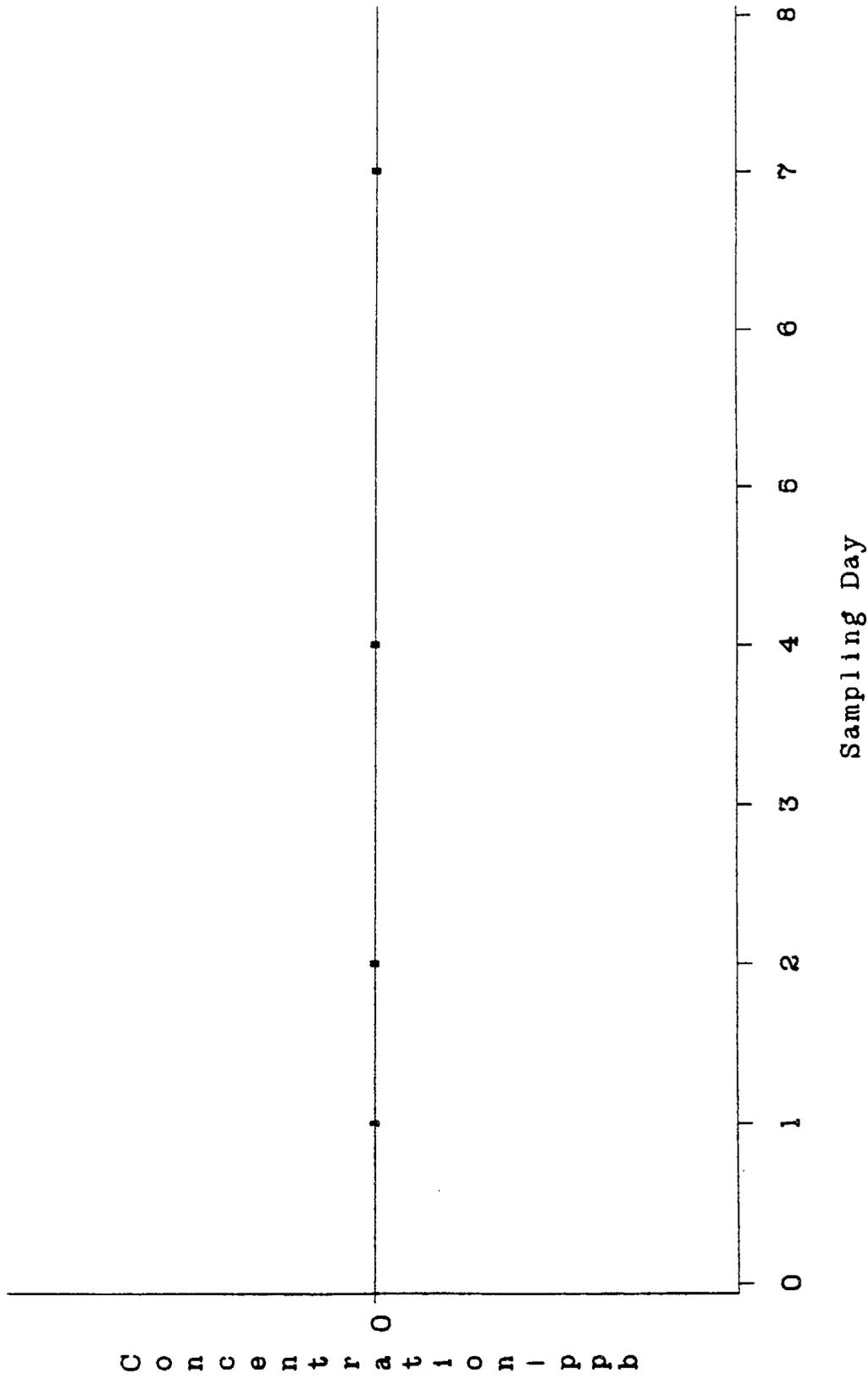
Concentration-ppb

Sampling Day

Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
             1=QC1   2=QC2   3=QC3

IB-4

#=9 Compound Name=dichloromethane

Concentration-ppb (vertical axis label)

Sampling Day (horizontal axis label)

Sample Type	A=BN1	B=BN2	C=BS1	D=BS2
	E=CB1	F=CB2	G=CS1	H=CS2
	1=QC1	2=QC2	3=QC3	

IB-5

#=11   Compound Name=1,1,2-trichloro-1,2,2-trifluoroethane

Concentration

0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00

Sampling Day

0   1   2   3   4   5   6   7   8

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2
              E=CB1   F=CB2   G=CS1   H=CS2
              1=QC1   2=QC2   3=QC3

IB-6

#=14   Compound Name=trichloromethane

Sampling Day

Concentration-ppb
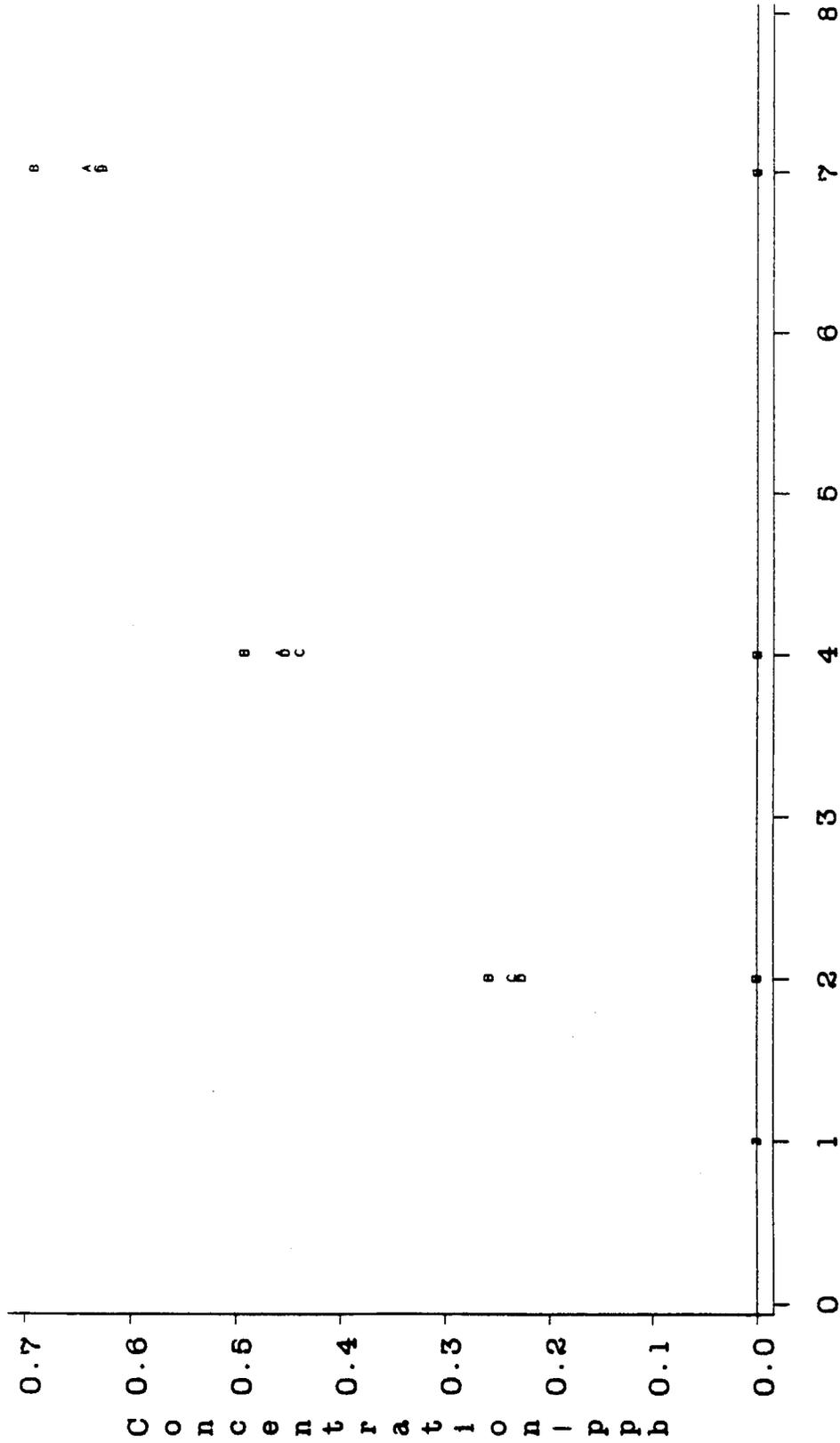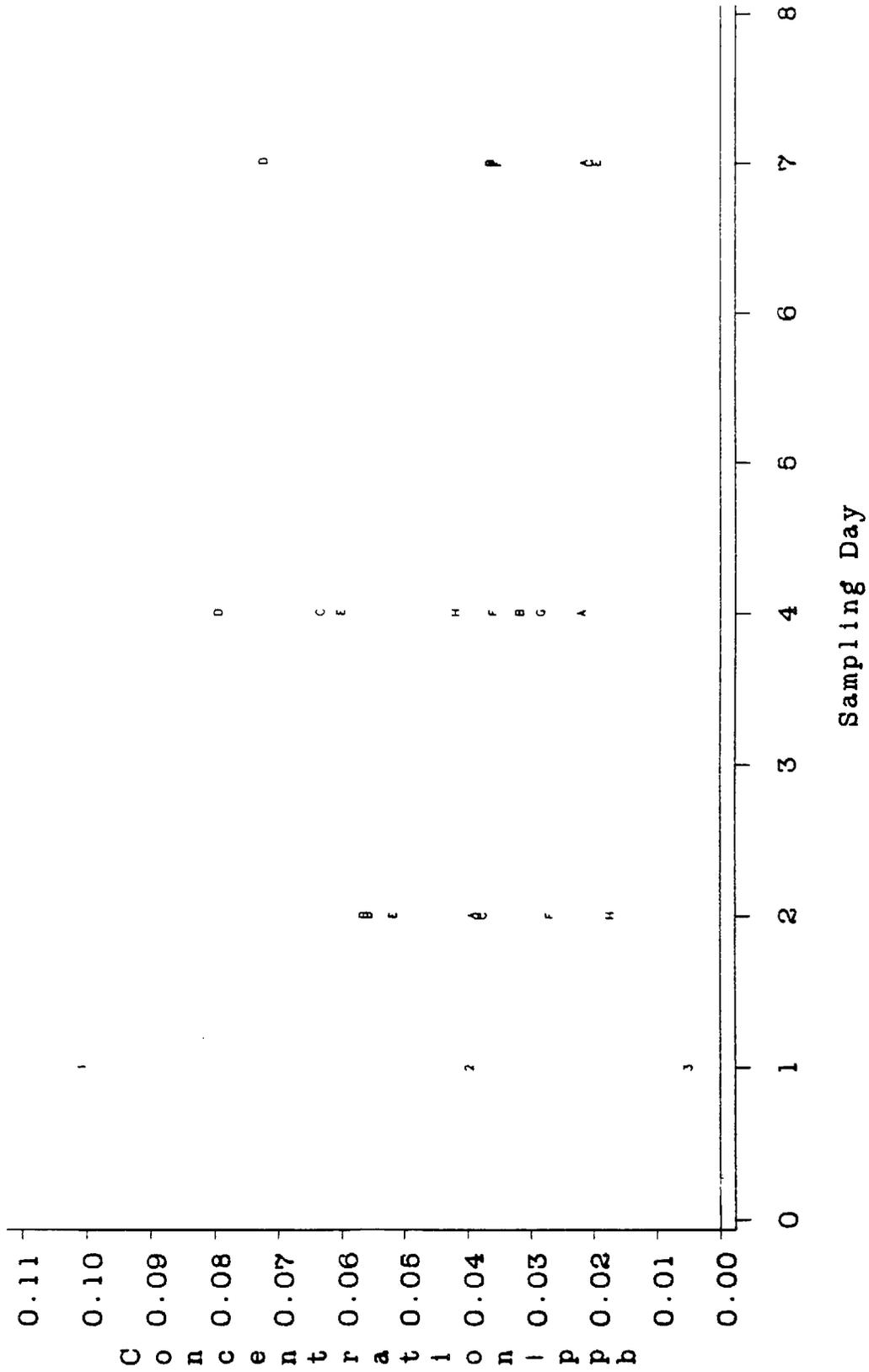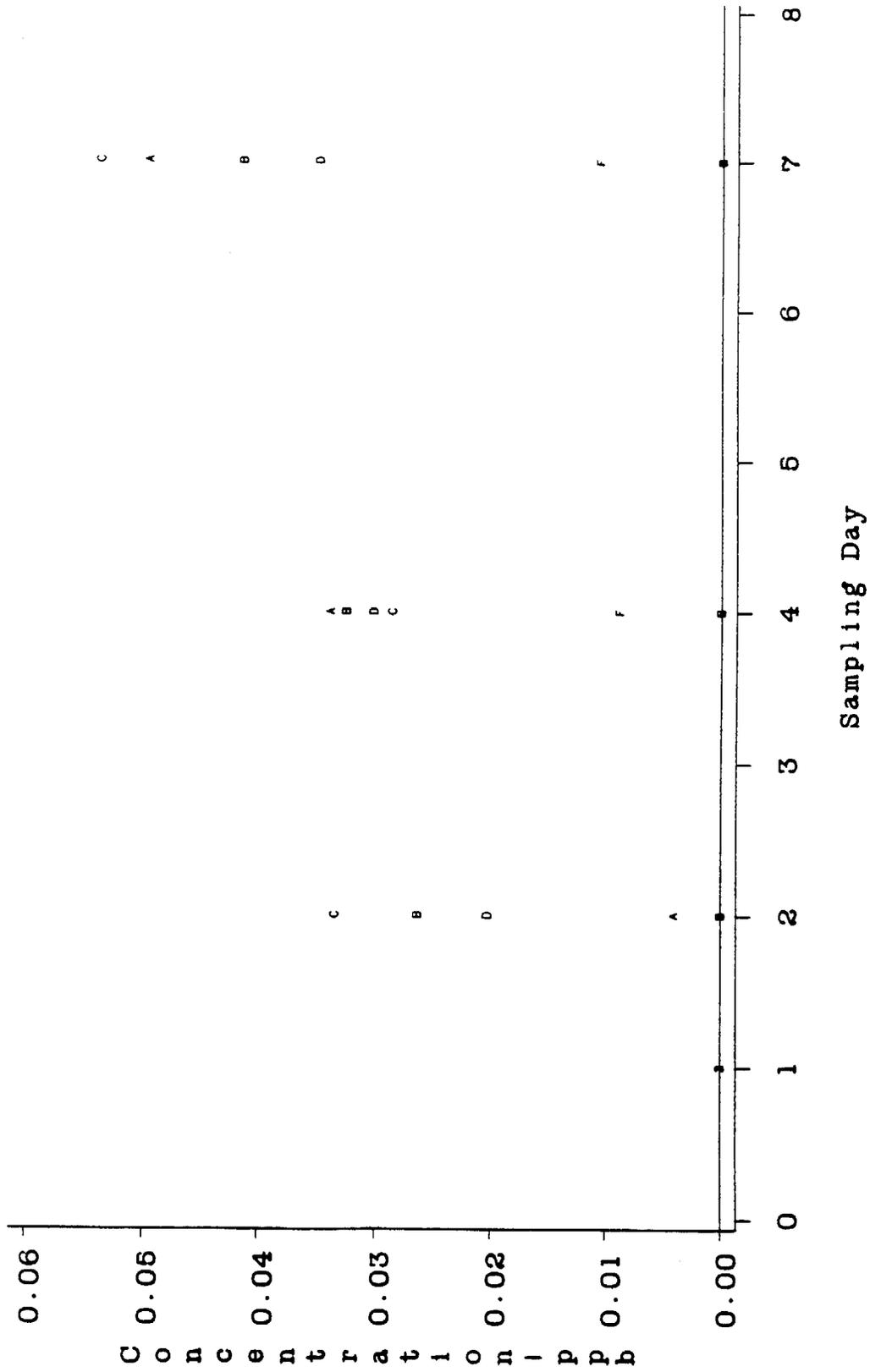
Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
             1=QC1   2=QC2   3=QC3

#=15   Compound Name=1,2-dichloroethane
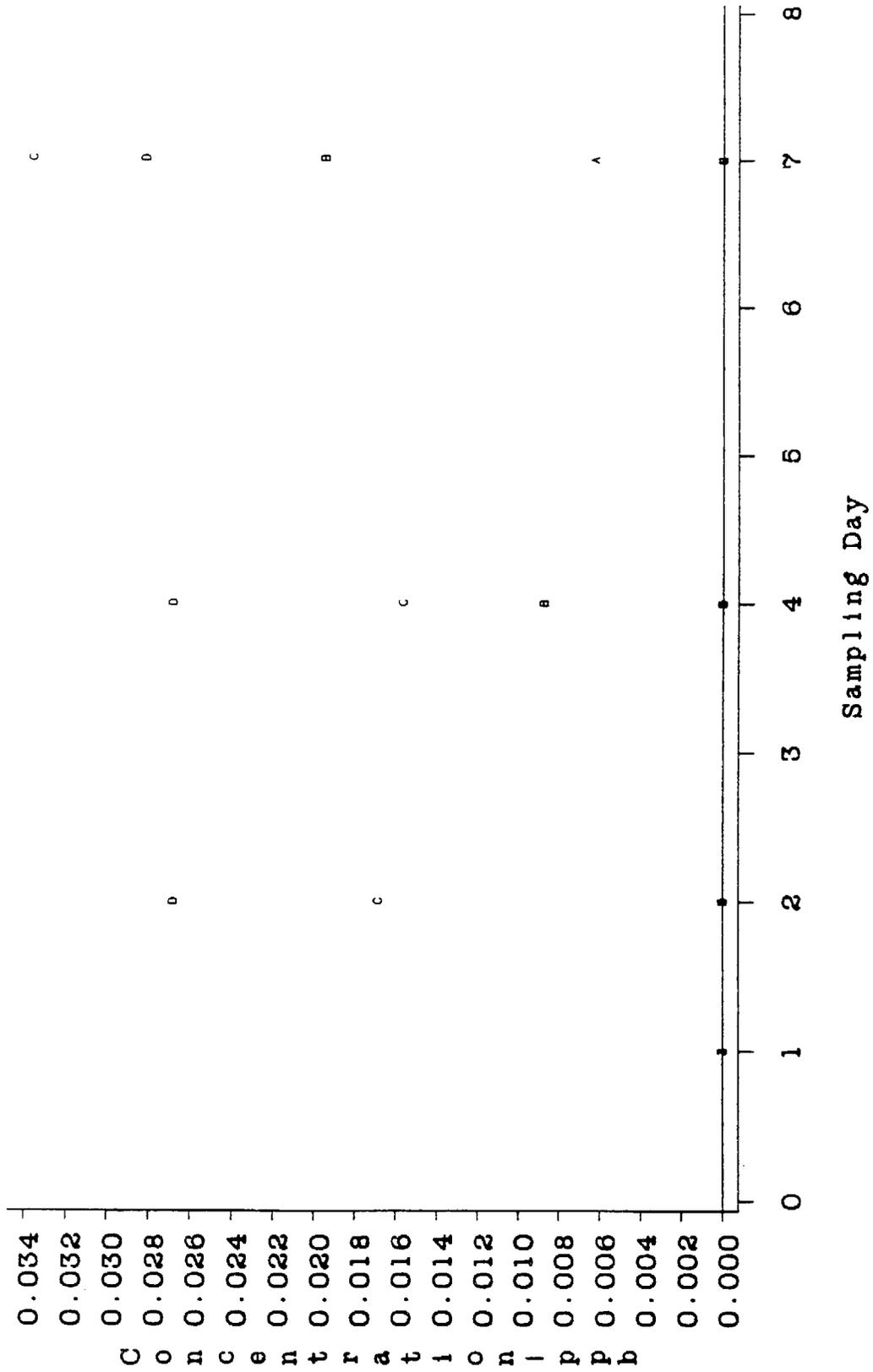
Concentration (ppm)

0.034
0.032
0.030
0.028
0.026
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000

0   1   2   3   4   5   6   7   8

Sampling Day

Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
             1=QC1   2=QC2   3=QC3

IB-8

#=16   Compound Name=1,1,1-trichloroethane

Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
             1=QC1   2=QC2   3=QC3
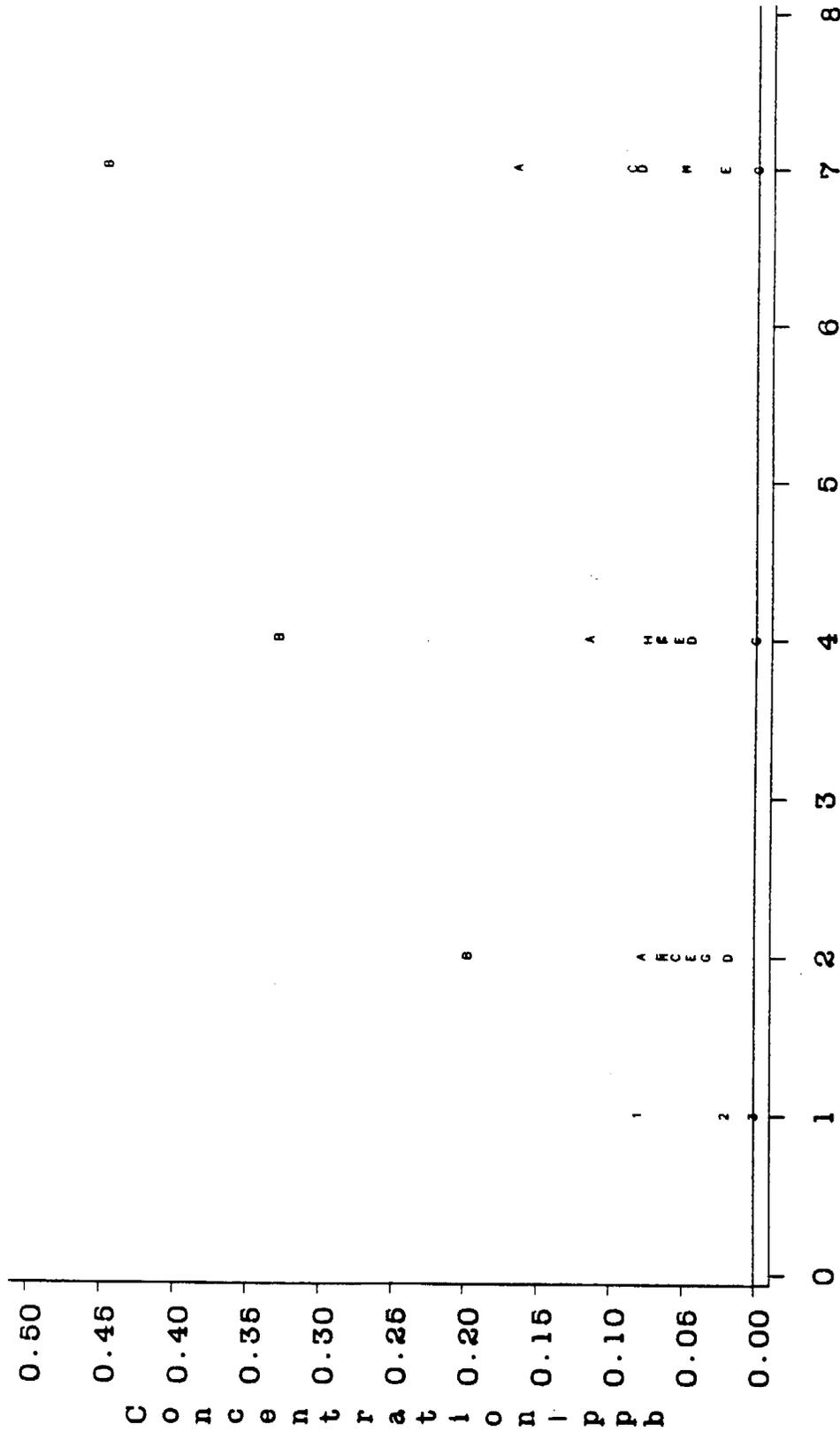
#=17 Compound Name=benzene

Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
             1=QC1   2=QC2   3=QC3

IB-10

#=18   Compound Name=carbon tetrachloride

Sampling Day

Concentration-ppb
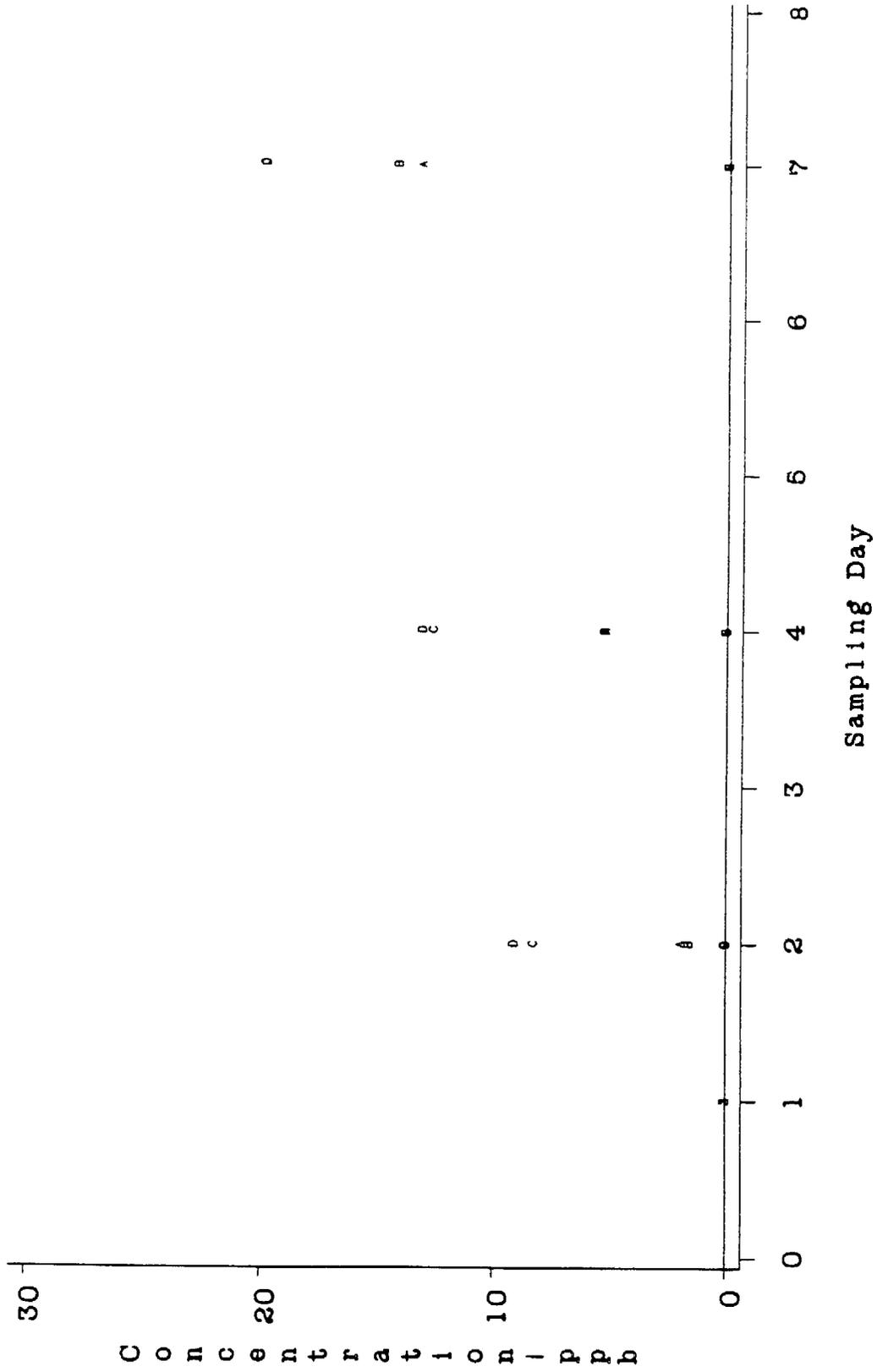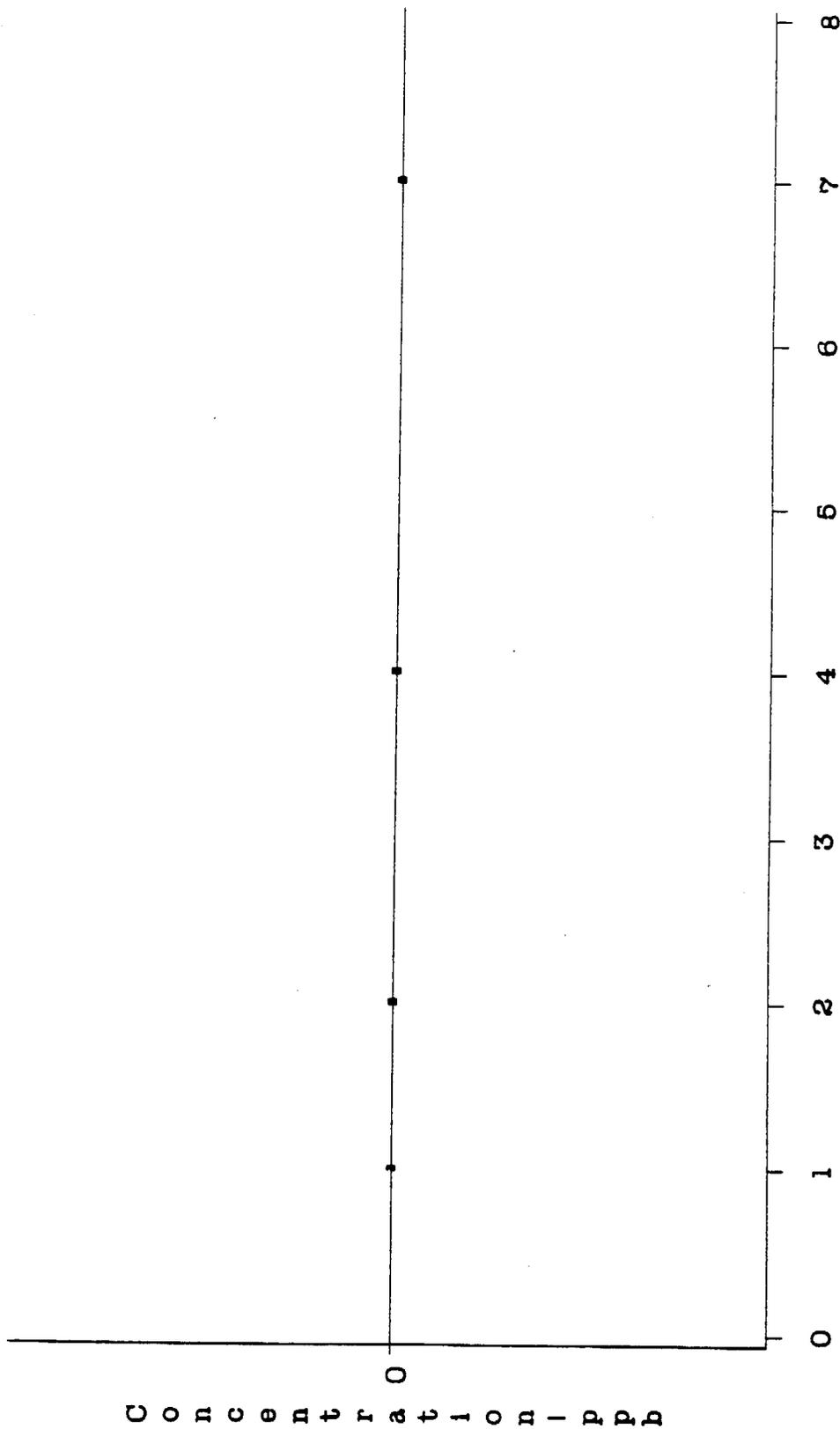
Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
             1=QC1   2=QC2   3=QC3

#=20   Compound Name=trichloroethene
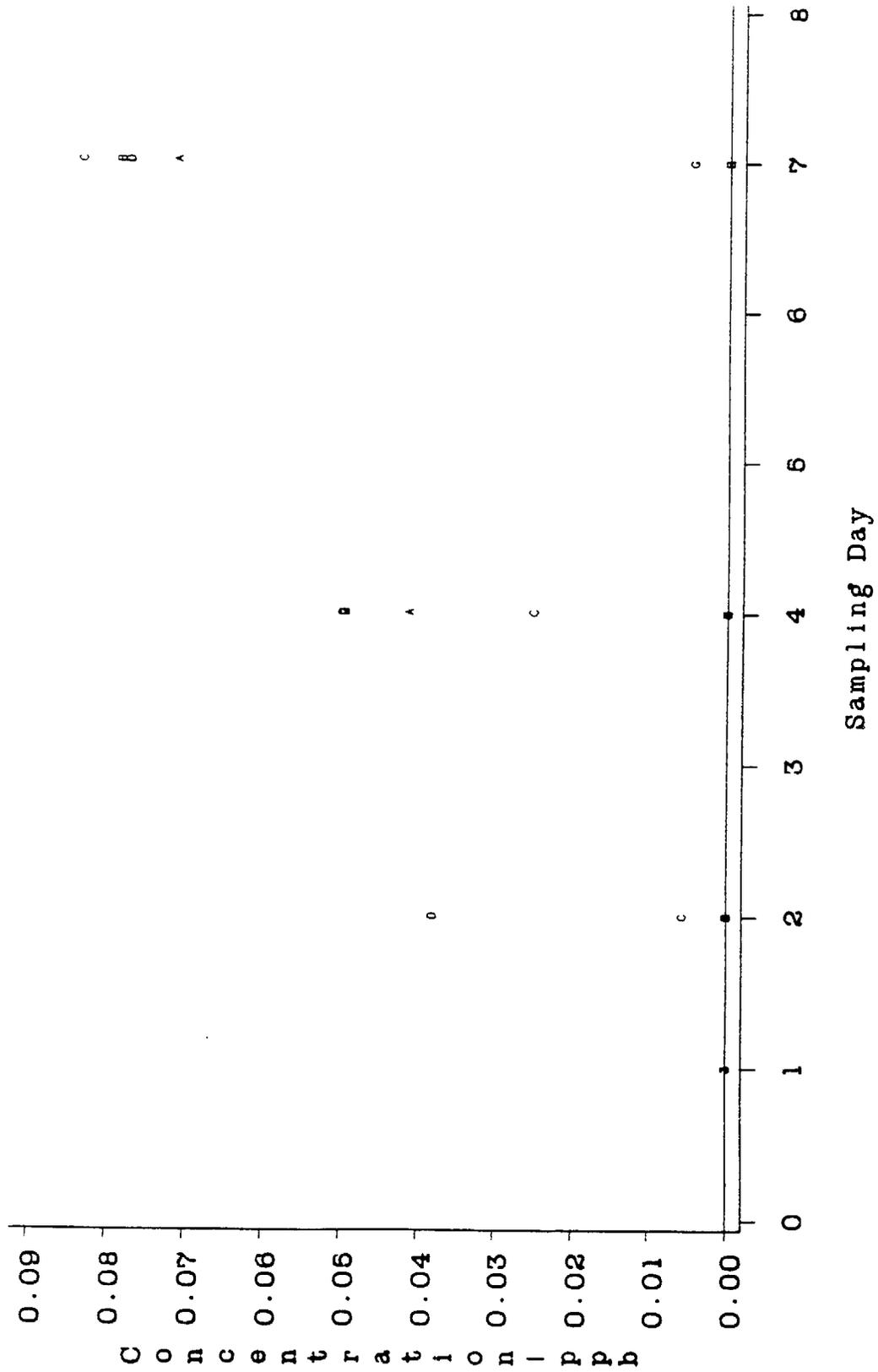
Concentration -ppb

0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00

0   1   2   3   4   5   6   7   8

Sampling Day

Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
             1=QC1   2=QC2   3=QC3

IB-12

#=24   Compound Name=toluene

Concentration-ppb
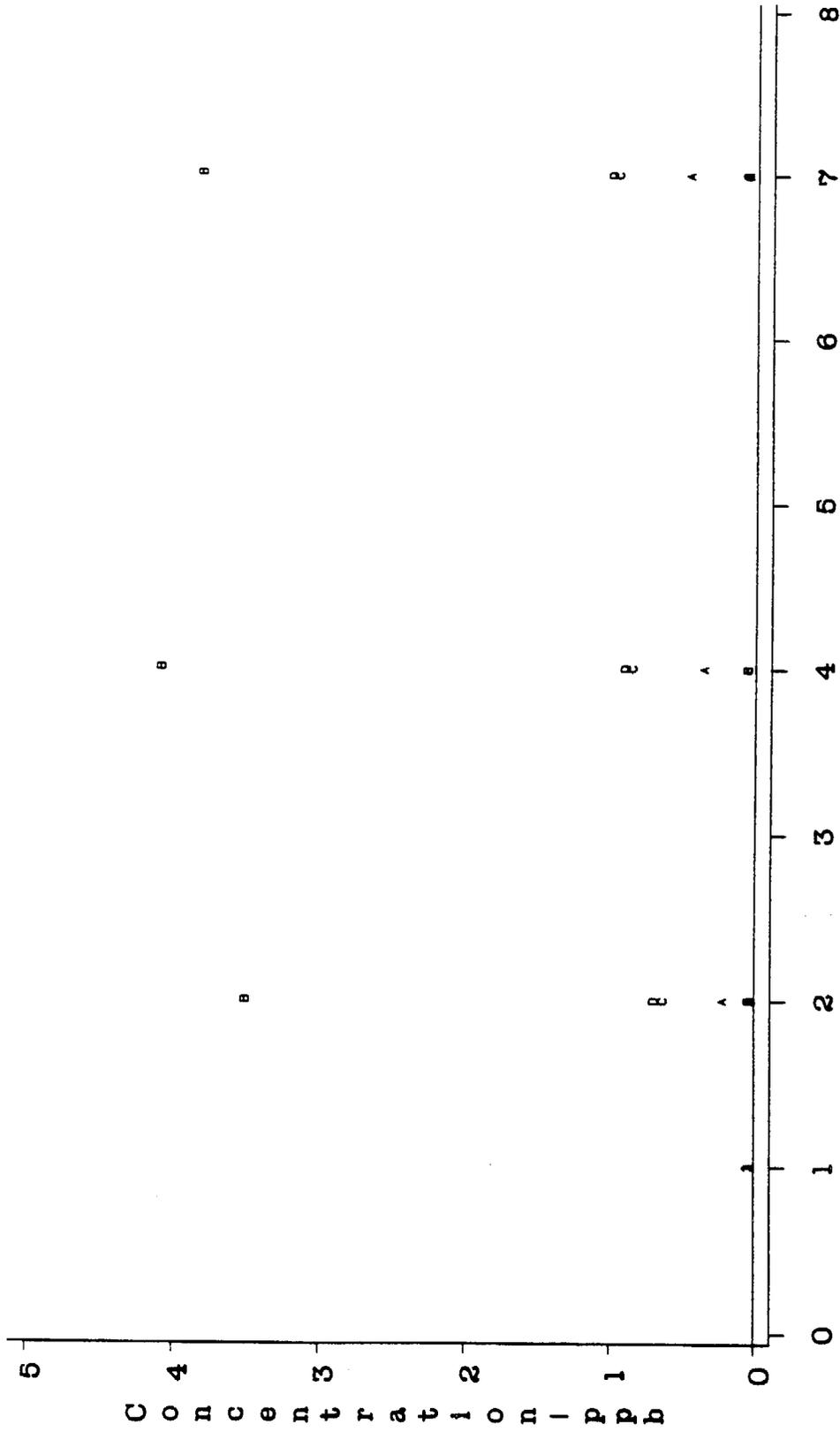
Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2
               E=CB1   F=CB2   G=CS1   H=CS2
               1=QC1   2=QC2   3=QC3

IB-13

#=25   Compound Name=1,2-dibromoethane

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2
               E=CB1   F=CB2   G=CS1   H=CS2
               1=QC1   2=QC2   3=QC3

Sampling Day

#=26   Compound Name=tetrachloroethene

Concentration-ppb

0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00

0   1   2   3   4   5   6   7   8

Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2
              E=CB1   F=CB2   G=CS1   H=CS2
              1=QC1   2=QC2   3=QC3

IB-15

#=29   Compound Name=m+p-xylene

Concentration-ppb

Sampling Day

Sample Type   A=BN1   B=BN2   C=BS1   D=BS2
              E=CB1   F=CB2   G=CS1   H=CS2
              1=QC1   2=QC2   3=QC3

IB-16

#=30   Compound Name=Styrene

Concentration-ppb

Sampling Day

Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
             1=QC1   2=QC2   3=QC3

IB-17

= 32   Compound Name=o-xylene

Sampling Day

Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
             1=QC1   2=QC2   3=QC3

IB-18

#=37   Compound Name=m-dichlorobenzene

Sampling Day

Concentration-ppb (vertical axis label)

0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00

0   1   2   3   4   5   6   7   8
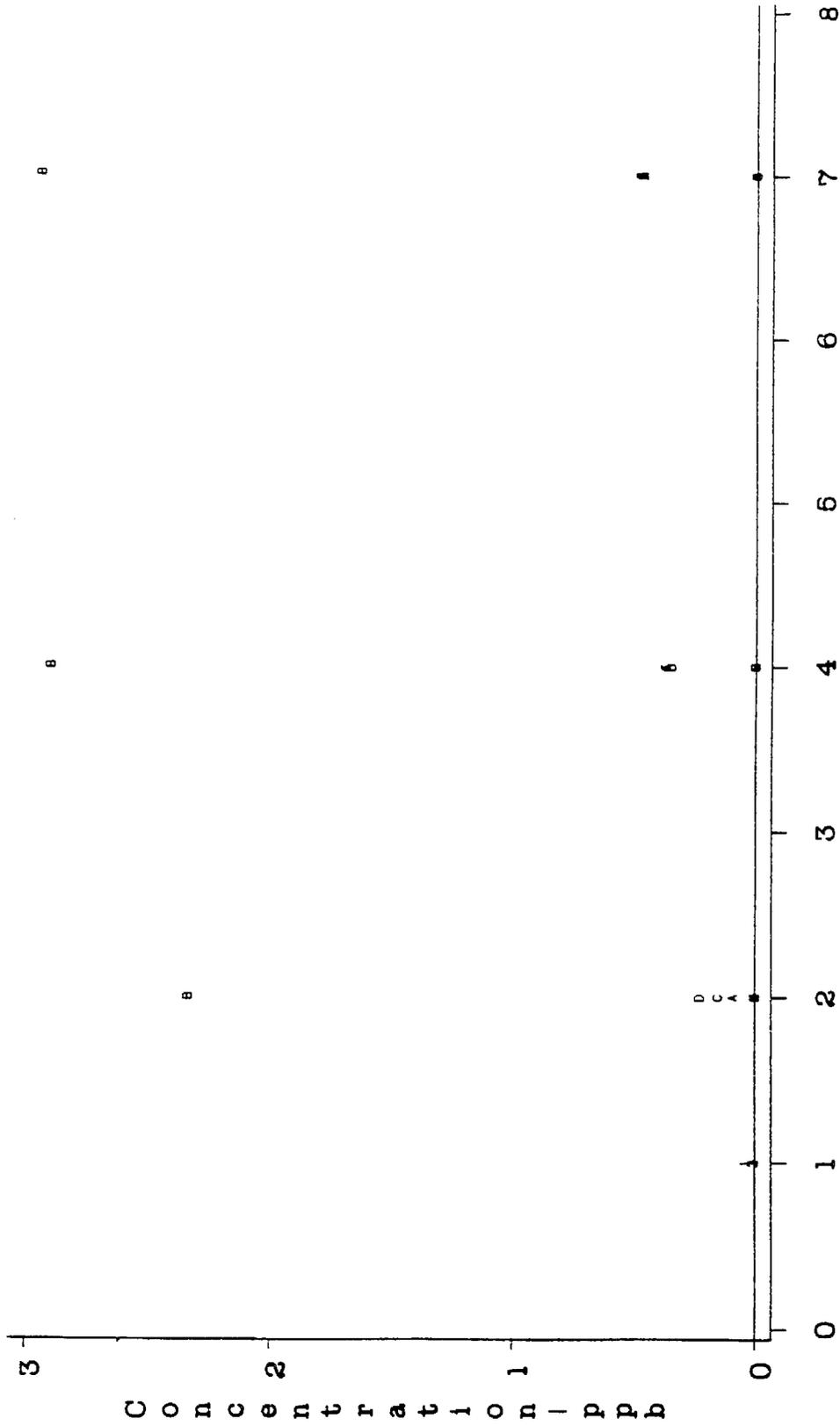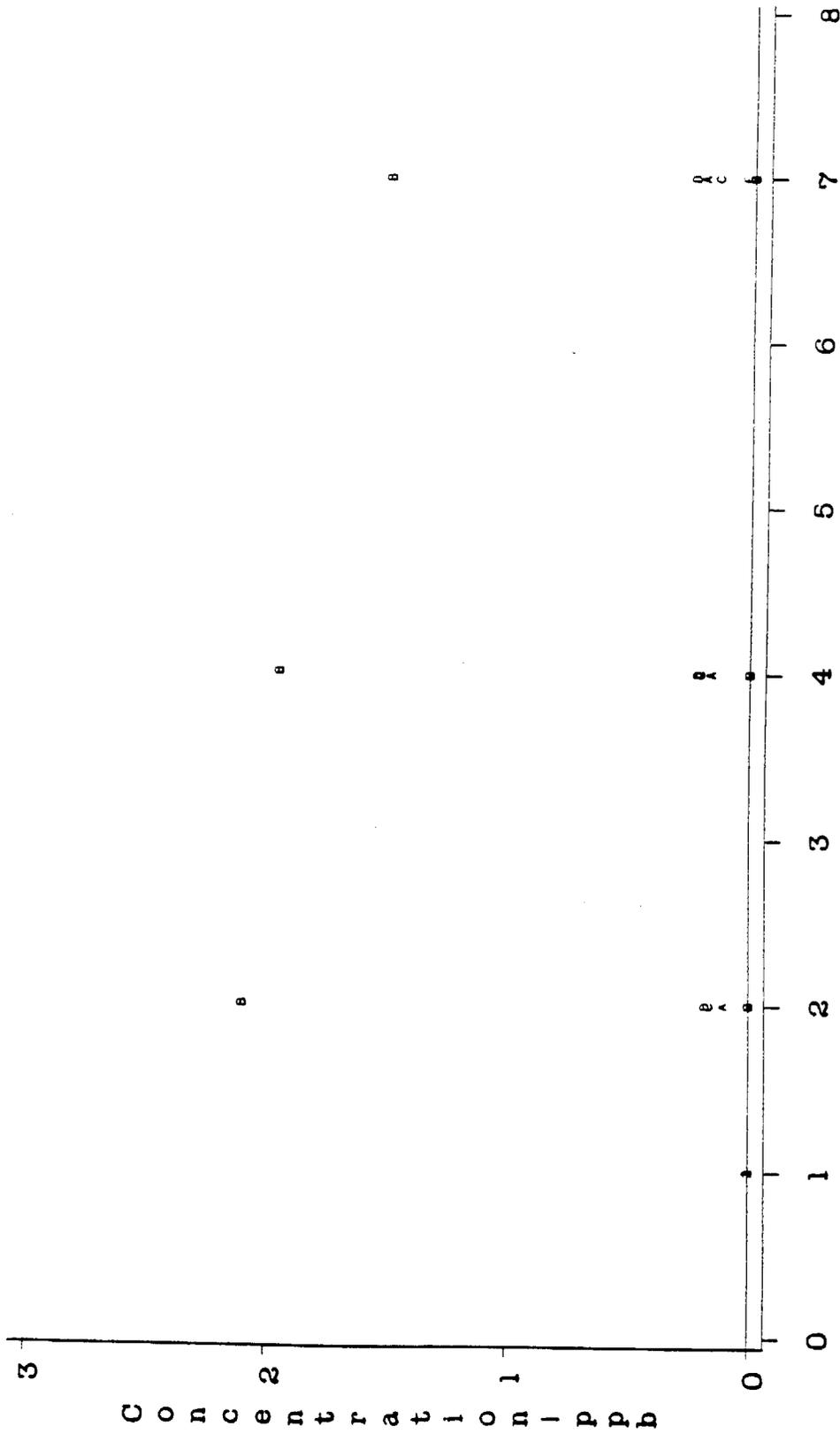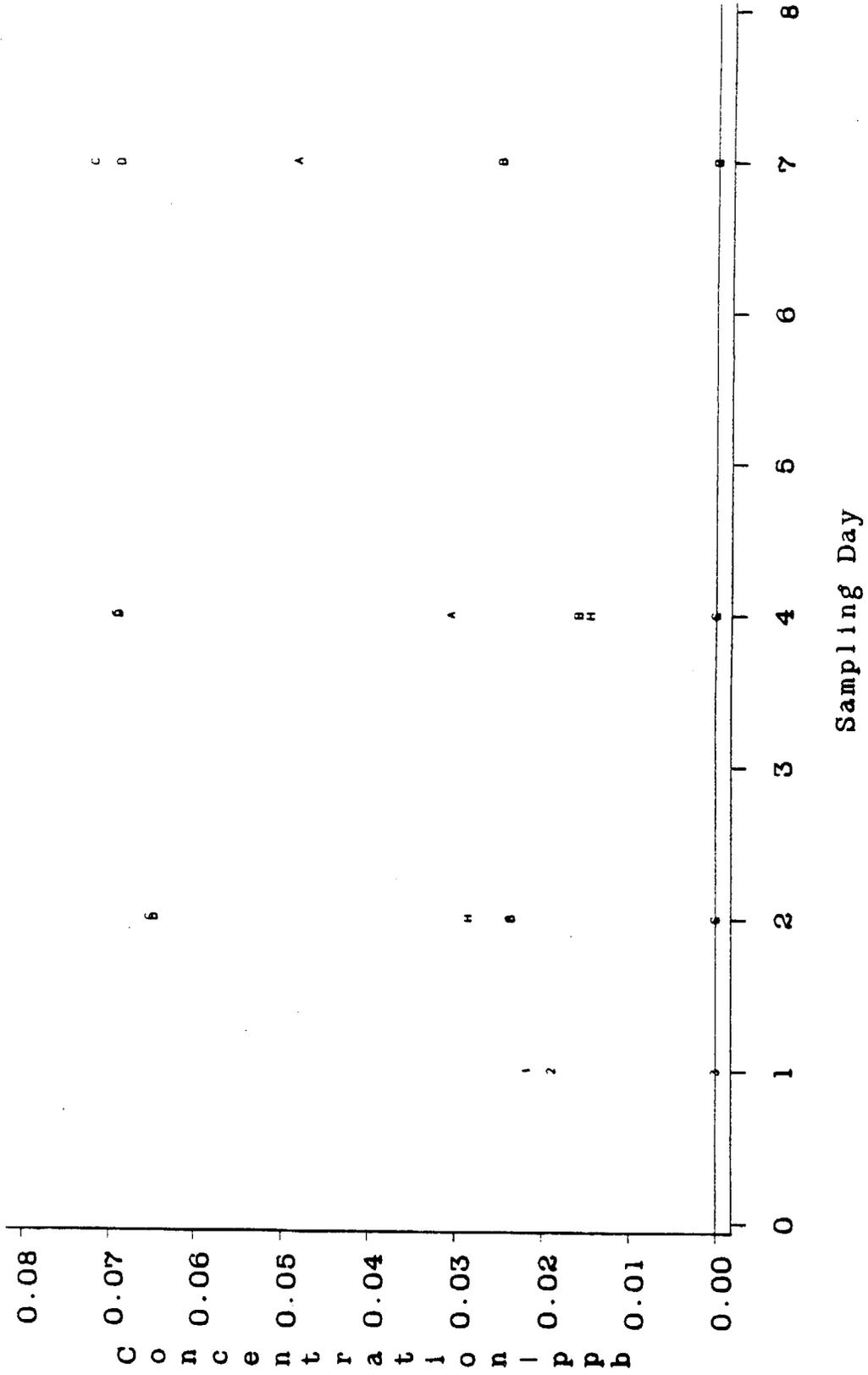
Sample Type   A=BN1   B=BN2   C=BS1   D=BS2
              E=CB1   F=CB2   G=CS1   H=CS2
   1=QC1   2=QC2   3=QC3

#=38   Compound Name=p-dichlorobenzene
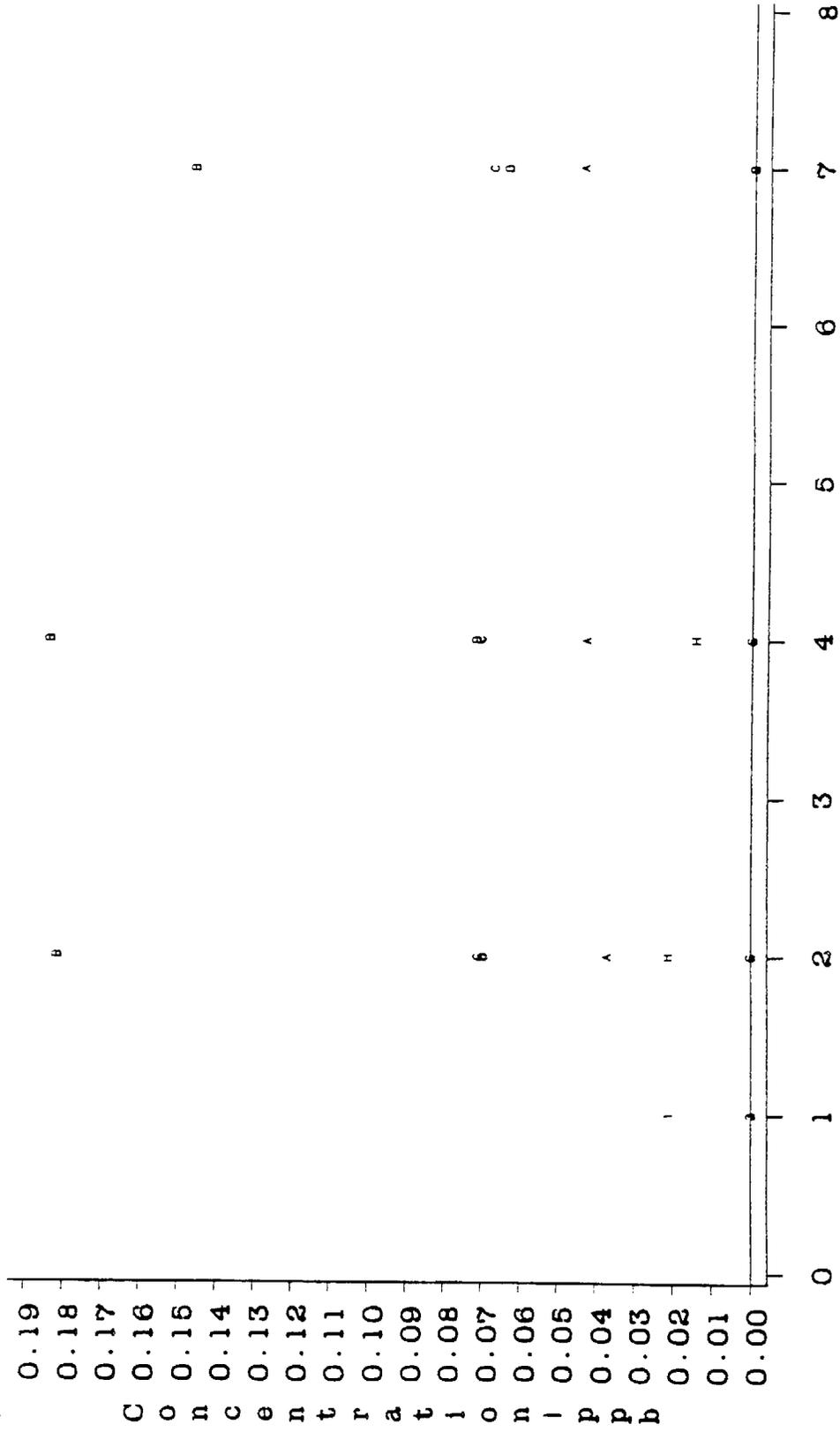
Sampling Day

Sample Type	A=BN1	B=BN2	C=BS1	D=BS2
E=CB1	F=CB2	G=CS1	H=CS2
1=QC1	2=QC2	3=QC3

#=39   Compound Name=o-dichlorobenzene
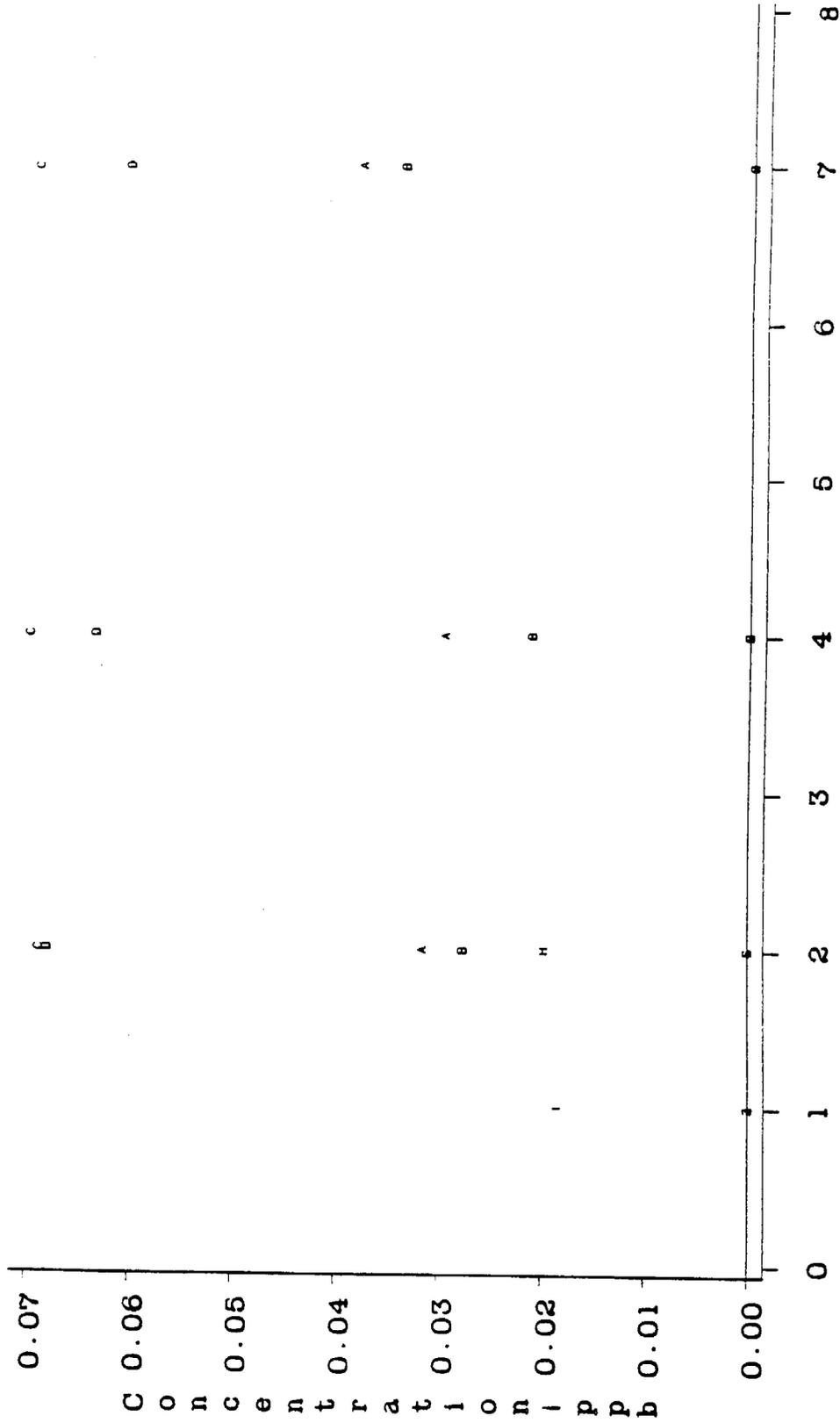
Sampling Day

Sample Type A=BN1   B=BN2   C=BS1   D=BS2
             E=CB1   F=CB2   G=CS1   H=CS2
   1=QC1   2=QC2   3=QC3

IB-21

APPENDIX II-A

DATA FROM ARB'S BAG SWAP STUDY

APPENDIX II-B

DATA FROM ARB'S BAG/CAN
COLLOCATED SAMPLES STUDY

DATA FROM ARB BAG/CAN
COLLOCATED SAMPLE STUDY

CHEMICAL	DATE	CONC (ppb)	
		BAG	CAN
DCM	861217	10.900	12.300
DCM	861230	2.200	1.300
DCM	870201	7.100	7.000
DCM	870224	2.300	1.200
DCM	870308	2.100	1.200
DCM	870326	4.800	2.900
DCM	870330	2.500	2.400
DCM	870405	1.700	1.400
DCM	870419	2.100	1.200
DCM	870428	2.800	1.900
DCM	870514	1.000	0.800
DCM	870519	1.100	0.700
DCM	870603	10.100	10.000
DCM	870615	1.900	1.300
DCM	870625	2.300	1.100
DCM	870708	.	.
DCM	870722	.	.
DCM	870730	3.000	3.800
DCM	870813	2.300	0.800
DCM	870819	1.700	3.600
DCM	870825	0.700	0.400
CHCL3	861217	0.100	1.000
CHCL3	861230	0.540	0.110
CHCL3	870201	0.100	0.110
CHCL3	870224	0.630	0.050
CHCL3	870308	0.040	0.050
CHCL3	870326	0.070	0.060
CHCL3	870330	0.060	0.080
CHCL3	870405	0.070	0.070
CHCL3	870419	0.070	0.090
CHCL3	870428	0.070	0.080
CHCL3	870514	0.030	0.110
CHCL3	870519	0.050	0.060
CHCL3	870603	0.070	0.070
CHCL3	870615	0.050	0.070
CHCL3	870625	0.060	0.050
CHCL3	870708	0.020	0.090
CHCL3	870722	0.130	0.120
CHCL3	870730	1.150	1.700
CHCL3	870813	0.070	0.090
CHCL3	870819	0.180	0.150
CHCL3	870825	0.090	0.080
EDC	861217	0.250	0.260
EDC	861230	.	.
EDC	870201	0.530	0.410
EDC	870224	.	.
EDC	870308	.	.
EDC	870326	.	.

DATA FROM ARB BAG/CAN
COLLOCATED SAMPLE STUDY

| CHEMICAL | DATE | CONC (ppb) | |
		BAG	CAN
EDC	870330	.	.
EDC	870405	.	.
EDC	870419	.	.
EDC	870428	1.600	1.900
EDC	870514	.	.
EDC	870519	.	.
EDC	870603	.	.
EDC	870615	0.610	0.880
EDC	870625	1.200	1.000
EDC	870708	.	.
EDC	870722	.	.
EDC	870730	0.360	0.320
EDC	870813	.	.
EDC	870819	0.740	1.600
EDC	870825	.	.
TCEA	861217	5.700	8.300
TCEA	861230	8.900	6.100
TCEA	870201	8.100	2.200
TCEA	870224	2.100	0.400
TCEA	870308	0.900	1.700
TCEA	870326	6.500	6.000
TCEA	870330	5.300	2.500
TCEA	870405	2.900	2.800
TCEA	870419	2.300	1.900
TCEA	870428	3.200	3.700
TCEA	870514	1.700	3.000
TCEA	870519	2.200	2.200
TCEA	870603	7.300	6.900
TCEA	870615	4.900	3.400
TCEA	870625	8.900	6.200
TCEA	870708	1.100	2.800
TCEA	870722	3.700	7.000
TCEA	870730	15.100	14.000
TCEA	870813	7.300	8.400
TCEA	870819	7.200	19.400
TCEA	870825	5.100	5.700
CCL4	861217	0.110	0.110
CCL4	861230	0.130	0.130
CCL4	870201	0.110	0.110
CCL4	870224	0.110	0.100
CCL4	870308	0.100	0.100
CCL4	870326	0.110	0.120
CCL4	870330	0.110	0.130
CCL4	870405	0.090	0.100
CCL4	870419	0.100	0.090
CCL4	870428	0.110	0.100
CCL4	870514	0.060	0.110
CCL4	870519	0.070	0.070

DATA FROM ARB BAG/CAN
COLLOCATED SAMPLE STUDY

CHEMICAL	DATE	CONC (ppb) BAG	CONC (ppb) CAN
CCL4	870603	0.100	0.100
CCL4	870615	0.090	0.090
CCL4	870625	0.100	0.070
CCL4	870708	0.040	0.120
CCL4	870722	0.130	0.230
CCL4	870730	1.100	0.160
CCL4	870813	0.170	0.180
CCL4	870819	0.200	0.240
CCL4	870825	0.140	0.180
TCE	861217	0.300	0.270
TCE	861230	0.400	0.310
TCE	870201	0.210	0.210
TCE	870224	0.100	0.060
TCE	870308	0.100	0.060
TCE	870326	0.220	0.150
TCE	870330	0.190	0.180
TCE	870405	0.100	0.080
TCE	870419	0.190	0.130
TCE	870428	0.100	0.070
TCE	870514	0.060	0.060
TCE	870519	0.080	0.030
TCE	870603	0.170	0.060
TCE	870615	0.130	0.050
TCE	870625	0.160	0.050
TCE	870708	0.100	0.050
TCE	870722	0.170	0.090
TCE	870730	0.290	0.160
TCE	870813	0.790	0.110
TCE	870819	0.410	0.210
TCE	870825	0.270	0.100
EDB	861217	.	.
EDB	861230	.	.
EDB	870201	.	.
EDB	870224	.	.
EDB	870308	.	.
EDB	870326	.	.
EDB	870330	.	.
EDB	870405	.	.
EDB	870419	.	.
EDB	870428	.	.
EDB	870514	.	.
EDB	870519	.	.
EDB	870603	.	.
EDB	870615	.	.
EDB	870625	.	.
EDB	870708	.	.
EDB	870722	.	.
EDB	870730	.	.

DATA FROM ARB BAG/CAN
COLLOCATED SAMPLE STUDY

| CHEMICAL | DATE | CONC (ppb) | |
		BAG	CAN
EDB	870813	.	.
EDB	870819	.	.
EDB	870825	0.016	0.011
PERC	861217	2.500	2.600
PERC	861230	3.100	2.600
PERC	870201	1.100	1.100
PERC	870224	0.330	0.260
PERC	870308	0.310	0.280
PERC	870326	1.080	1.040
PERC	870330	1.110	1.140
PERC	870405	0.430	0.430
PERC	870419	0.530	0.300
PERC	870428	0.870	0.910
PERC	870514	0.400	0.670
PERC	870519	0.270	0.250
PERC	870603	1.250	1.100
PERC	870615	0.670	0.650
PERC	870625	1.100	0.630
PERC	870708	0.370	0.930
PERC	870722	0.790	1.300
PERC	870730	1.750	2.100
PERC	870813	0.750	0.680
PERC	870819	1.250	2.400
PERC	870825	0.890	0.930
BENZ	861217	7.500	7.600
BENZ	861230	9.000	9.500
BENZ	870201	7.600	8.200
BENZ	870224	1.600	1.900
BENZ	870308	2.300	2.100
BENZ	870326	3.800	3.600
BENZ	870330	3.500	3.900
BENZ	870405	2.900	3.200
BENZ	870419	2.700	3.300
BENZ	870428	1.600	1.800
BENZ	870514	2.100	2.400
BENZ	870519	1.300	1.400
BENZ	870603	2.800	3.100
BENZ	870615	2.100	2.300
BENZ	870625	1.900	2.100
BENZ	870708	1.200	1.900
BENZ	870722	3.100	3.200
BENZ	870730	5.900	6.500
BENZ	870813	1.500	2.100
BENZ	870819	2.800	2.800
BENZ	870825	2.500	2.800